

Interpretation of the Cu K-edge EXAFS spectra of Cu₃N using ab initio molecular dynamics

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Abstract

Cubic copper nitride (Cu₃N) has anti-perovskite structure, and its properties are strongly affected by anisotropic thermal vibrations of copper atoms. *Ab initio* molecular dynamics (AIMD) simulations were performed in the temperature range from 300 K to 700 K in order to probe the details of Cu₃N lattice dynamics. The Cu K-edge extended X-ray absorption fine structure (EXAFS) spectrum of bulk Cu₃N was used to validate AIMD simulations at 300 K. The AIMD results suggest strong anharmonicity of the Cu–N and Cu–Cu bonds, the rigidity of NCu₆ octahedra and strong correlation in atomic motion within –N–Cu–N– atom chains as well as support anisotropy of copper thermal vibrations.

Keywords: Copper nitride, Cu₃N, Extended X-ray absorption fine structure (EXAFS), Ab initio molecular dynamics

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1. Introduction

Copper nitride (Cu₃N) has a cubic anti-ReO₃-type structure (Fig. 1) composed of the NCu₆ octahedra joined by corners (Zachwieja and Jacobs, 1990; Paniconi et al., 2007). Opposite to metallic ReO₃, pure Cu₃N is a narrow band gap ($E_g=1.1-1.8$ eV) semiconductor (Jiang et al., 2018). Cu₃N is potentially interesting candidate for many applications such as write-once read-many (WORM) optical storage devices (Asano et al., 1990; Maruyama and Morishita, 1996), non-volatile magnetic random access memories (Borsa et al., 2002) and optical lithography for a fabrication of microscopic metal links (Maya, 1993; Borsa and Boerma, 2004). Electro-catalytic properties of copper nitride in alkaline fuel cells were also reported (Wu and Chen, 2011). Cu₃N usage as an absorber for photovoltaic and photo-electrochemical solar cells was recently reported (Zakutayev et al., 2014; Caskey et al., 2014).

The dynamic properties of Cu₃N lattice are determined by anisotropic thermal vibrations of copper atoms, having larger amplitude orthogonal to linear -N-Cu-N- atomic chains (Zachwieja and Jacobs, 1990). X-ray absorption spectroscopy is ideally suited to probe in-situ local atomic structure and lattice dynamics of Cu₃N (Kuzmin et al., 2016b; Timoshenko et al., 2017). It was shown previously based on the results of reverse Monte Carlo calculations (Timoshenko et al., 2016, 2017) that the anisotropy of copper atom vibrations is enhanced upon increasing temperature and is accompanied by tilting motion of NCu₆ octahedra. Strong correlation in the motion of atoms was observed along -N-Cu-N- atomic chains but it reduced with an increase of interatomic distance. Finally, it was found that anticorrelated motion of nearest Cu atoms indicates on breathing-type motion of NCu₆ octahedra.

Another atomistic simulation approach to the interpretation of EXAFS utilizes molecular dynamics (MD) simulations (D'Angelo et al., 1994, 1996; Palmer et al., 1996). The MD-EXAFS method is especially useful for the analysis of EXAFS in crystalline materials where outer shell and multiple-scattering (MS) contributions are significant and overlap (Kuzmin and Evarestov, 2009; Kuzmin et al., 2016a; Bocharov et al., 2016). Besides, the method can be employed to validate the interatomic potential models used in the classical MD simulations (Kuzmin et al., 2016a; Bocharov et al.,

2017).

In the MD-EXAFS method, the structural model of a material is constructed first, taking into account periodicity, chemical composition as well as the particle size and shape in the case of nanomaterials. One should also define the interaction potential model, which can be based on empirical force-field or calculated from first-principles. Next, the MD simulation is performed at the required temperature and pressure, providing a set of instantaneous atomic configurations (“snapshots”), which represent a time-dependent evolution of the material structure. The use of Newtonian dynamics restricts the application of MD at low temperatures, where the quantum zero-point motion of atoms becomes important. Nevertheless, MD method usually performs well at high temperatures and, thus, is suitable to model the anharmonic thermal motion of atoms. When the MD simulation is done, the accumulated coordinates of atoms can be used to evaluate different structural properties as, for example, the radial distribution functions, the mean interatomic distances and angles, the mean-square relative displacements, etc. Moreover, a set of EXAFS spectra can be calculated for each of the atomic configurations within ab initio MS formalism, and the configuration-averaged EXAFS spectrum can be readily compared with the experiment to validate the MD simulation.

The MD-EXAFS approach, based on classical MD simulations, has been successfully applied previously to a number of perovskite-type materials as SrTiO₃ (Kuzmin and Evarestov, 2009; Kuzmin et al., 2016a), ReO₃ (Kalinko et al., 2009), LaCoO₃ (Kuzmin et al., 2011) and ScF₃ (Bocharov et al., 2016). Some preliminary results have been also obtained for Cu₃N (Timoshenko et al., 2016).

In this study, we performed systematic *ab initio* molecular dynamics (AIMD) simulations of bulk Cu₃N in the temperature range from 300 K to 700 K in order to elucidate the details of lattice dynamics and anharmonicity of the Cu–N and Cu–Cu bonding.

2. Experimental

The room temperature Cu K-edge X-ray absorption spectrum (Fig. 2) of commercial polycrystalline Cu₃N powder (99.5%, Alfa Aesar) was acquired in transmission

mode at the bending magnet beamline C (Rickers et al., 2007) at HASYLAB/DESY synchrotron radiation facility. The details of the experiment and data treatment were published previously (Kuzmin et al., 2016b; Timoshenko et al., 2017).

3. Computational details

The AIMD simulations of bulk Cu₃N were performed based on Kohn-Sham density functional theory (DFT) within the isobaric-isothermal (NpT) ensemble. The QUICKSTEP module (VandeVondele et al., 2005) of the CP2K code (CP2K developers group, 2000–2018) was employed for all AIMD runs using the Cray XC50 system “Piz Daint” at the Swiss National Supercomputing Centre (CSCS). Goedecker-Teter-Hutter (GTH) pseudopotentials (semi-core GTH PP for Cu) (Krack, 2005) and contracted Gaussian basis sets of double-zeta quality specifically optimised for the use with the GTH pseudopotentials in the framework of CP2K for condensed phase systems (DZVP, MOLOPT-SR) (VandeVondele and Hutter, 2007) were employed in all runs.

NpT ensemble AIMD was conducted at four temperatures: 300, 450, 600, and 700 K. A thermalisation run of about 15 ps duration was performed at each temperature to equilibrate the supercell $5a_0 \times 5a_0 \times 5a_0$ ($a_0 = 3.819 \text{ \AA}$ is the lattice parameter) Cu₃N model system with periodic boundary conditions at the actual target temperature. This supercell size is large enough to avoid artefacts in the EXAFS spectra during the MD-EXAFS analysis (Kuzmin and Evarestov, 2009) in the post-processing phase. Finally, the equilibrated systems were used in the production runs of about 30 ps duration at the each target temperature.

Sets of atomic coordinates obtained as a result of the AIMD simulations were used to calculate the radial distribution functions (RDFs) and the mean-square relative displacements (MSRD) (also known as Debye-Waller factors) for Cu–N and Cu–Cu atom pairs. The average bond angles and the bond angles between the average positions of Cu and N atoms were also evaluated.

Sets of atomic configurations obtained in the AIMD simulations were used to calculate the configuration-averaged Cu K-edge EXAFS $\chi(k)$ (k is the photoelectron wavenumber) within the multiple-scattering (MS) approach (Kuzmin and Evarestov,

2009; Kuzmin et al., 2016a) using *ab initio* self-consistent real-space MS FEFF8.50L code (Ankudinov et al., 1998; Rehr and Albers, 2000). The scattering potential and partial phase shifts were calculated only once for the cluster with the radius of 8 Å, centered at the absorbing Cu atom and constructed based on the crystallographic Cu₃N structure. The photoelectron inelastic losses were accounted using the complex exchange-correlation Hedin-Lundqvist potential (Hedin and Lundqvist, 1971).

4. Results

The experimental and calculated (using NpT ensemble AIMD) Cu K-edge EXAFS spectra of bulk Cu₃N at 300 K and their Fourier transforms (FTs) are compared in Fig. 2. The overall agreement between theory and experiment is quite good. The frequency of the EXAFS signals and the related positions of peaks in FTs are well reproduced by the simulations. However, the amplitudes of the FT peaks at 2.3 Å and 3.4 Å are larger in the simulated signal indicating that thermal disorder is underestimated in the second and third coordination shells.

Atomic configurations produced in the AIMD simulations of Cu₃N can be used to extract a number of structural parameters and their temperature dependencies.

In Fig. 3 the calculated radial distribution functions (RDFs) $G(R)$ around the absorbing atom Cu₀ are shown in the region of the nearest two shells, corresponding to Cu₀-N₁ and Cu₀-Cu₂ atom pairs. The asymmetric shape of the two peaks at ~1.9 Å and ~2.7 Å suggests a strong anharmonicity of the atomic vibrations in Cu₃N.

The temperature dependencies of the mean-square relative displacements (MSRD) for the first seven coordination shells of the absorbing Cu₀ atom are shown in Fig. 4 for Cu-N and Cu-Cu atom pairs. The results of reverse Monte Carlo (RMC) analysis of low-temperature (10-300 K) EXAFS data are also given for comparison (Timoshenko et al., 2017). The two sets of MSRD data match each other at 300 K. The temperature dependencies of the MSRD factors for Cu₀-N₁, Cu₀-N₄, Cu₀-Cu₂ and Cu₀-Cu₆ atom pairs agree well between low-temperature experimental and high-temperature calculated values. At the same time, the AIMD calculated MSRD factors for Cu₀-N_{7b}, Cu₀-Cu_{3b} and Cu₀-Cu₅ atom pairs are overestimated, but for Cu₀-N_{7a} and Cu₀-Cu_{3b}

atom pairs are slightly underestimated. Thus, overall, the AIMD calculations are able to describe the structure and dynamics of bulk Cu₃N.

It is important that analysis of atomic coordinates allows us to separate atom pairs having similar interatomic distances as Cu₀-N_{7a} and Cu₀-N_{7b} or Cu₀-Cu_{3a} and Cu₀-Cu_{3b} (Fig. 1). Small values of MSRDS for Cu-N₁, Cu-Cu_{3a} and Cu-N_{7a} atom pairs relative to others suggest strong correlation in atomic motion along crystallographic axes within -Cu-N-Cu-N- atomic chains. Moreover, the MSRDS factors for Cu₀-Cu_{3b} are much larger than those for Cu₀-Cu_{3a}, indicating anisotropic thermal vibration of Cu atoms, with the amplitude being larger in the direction orthogonal to -N-Cu-N- chains.

Temperature dependencies of several bond angles are shown in Figs. 5, 6 and 7. Here we distinguish between the average values of bond angles ($\langle \rangle$), seen by EXAFS, and the angle values between the average positions of atoms ($\langle \rangle$ - $\langle \rangle$ - $\langle \rangle$), seen by diffraction. A strong difference between these two cases was observed for N₁-Cu_{3a}-N_{7a}, Cu₀-N₁-Cu_{3a} and Cu₀-Cu₂-Cu₆ angles, whereas no or very small difference was detected for Cu₀-N₁-Cu₂ and Cu₀-Cu₂-Cu_{3a} angles.

The anisotropic vibrational amplitude of Cu atoms is responsible for a decrease of the average values of N₁-Cu_{3a}-N_{7a} and Cu₀-N₁-Cu_{3a} angles by about 5–15°. At the same time, the rigidity of NCu₆ octahedra is supported by a stability of Cu₀-N₁-Cu₂ and Cu₀-Cu₂-Cu_{3a} angles being close to 90°. Finally, a dynamical tilting of NCu₆ octahedra can be deduced from a behaviour of Cu₀-Cu₂-Cu₆ angle together with the large MSRDS for Cu₀-Cu_{3b}.

5. Conclusion

Ab initio molecular dynamics simulations of cubic anti-perovskite copper nitride were performed within the NpT ensemble in the temperature range between 300 and 700 K. The AIMD results were validated using the MD-EXAFS approach by direct comparison with the Cu K-edge EXAFS of polycrystalline Cu₃N at 300 K. The simulations predict strong anharmonicity of Cu-N and Cu-Cu bonds, anisotropy of Cu atoms vibrations, the rigidity of NCu₆ octahedra and strong correlation in atomic mo-

tion within –N–Cu–N– atom chains. These findings are in agreement with the reverse Monte Carlo analysis of low-temperature (10–300 K) EXAFS data (Timoshenko et al., 2017).

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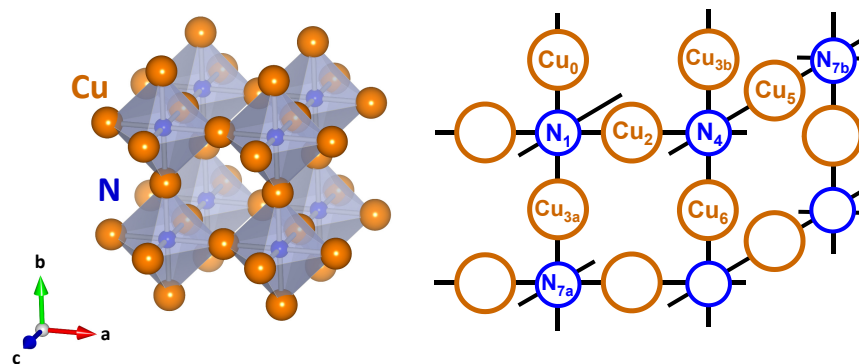


Figure 1: Crystal structure of cubic Cu₃N composed of regular NCu₆ octahedra (left panel). Fragment of Cu₃N structure with the labelled atoms of the first seven coordination shells around the absorbing copper atom Cu₀ (right panel). Non-equivalent atoms located at the same distance from the absorbing one are denoted by (a) and (b).

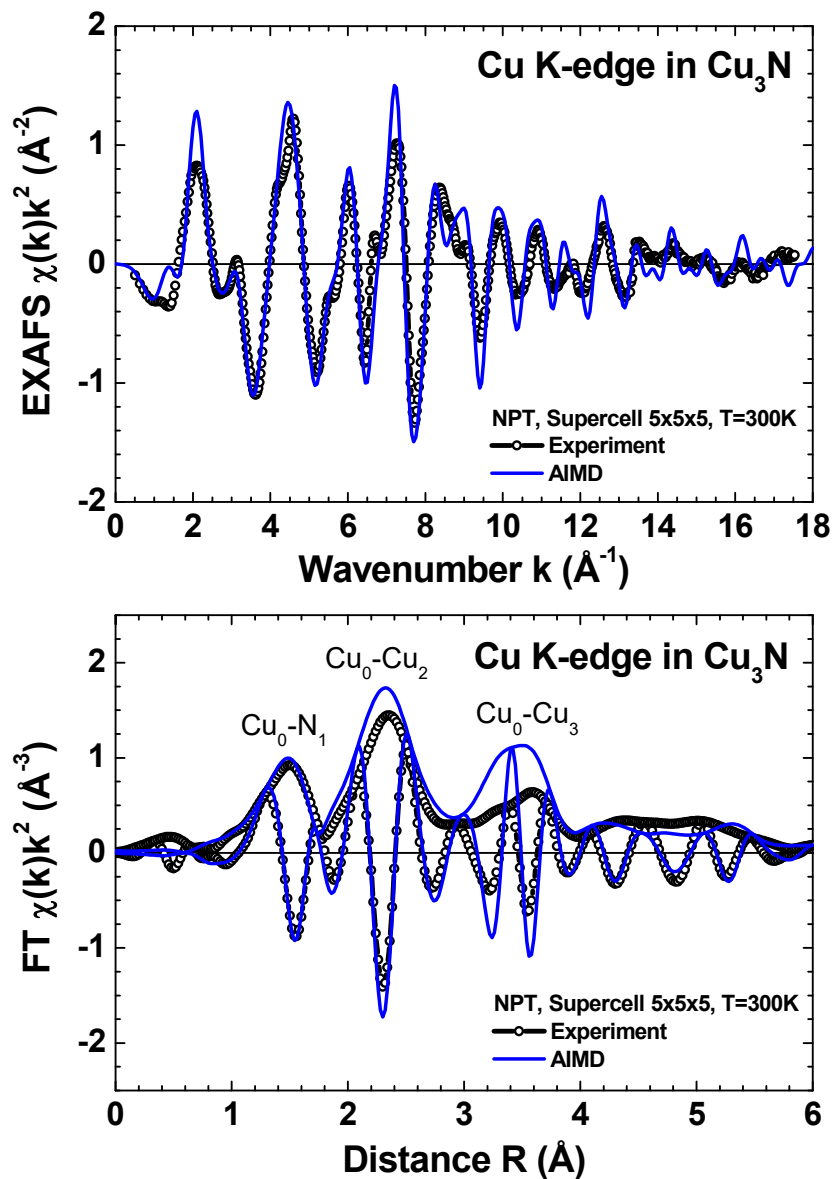


Figure 2: The experimental and AIMD calculated Cu K-edge EXAFS spectra (top panel) and their Fourier transforms (FTs) (bottom panel) at 300 K. The three peaks in FTs corresponding to the three nearest coordination shells, composed of nitrogen and copper atoms are indicated.

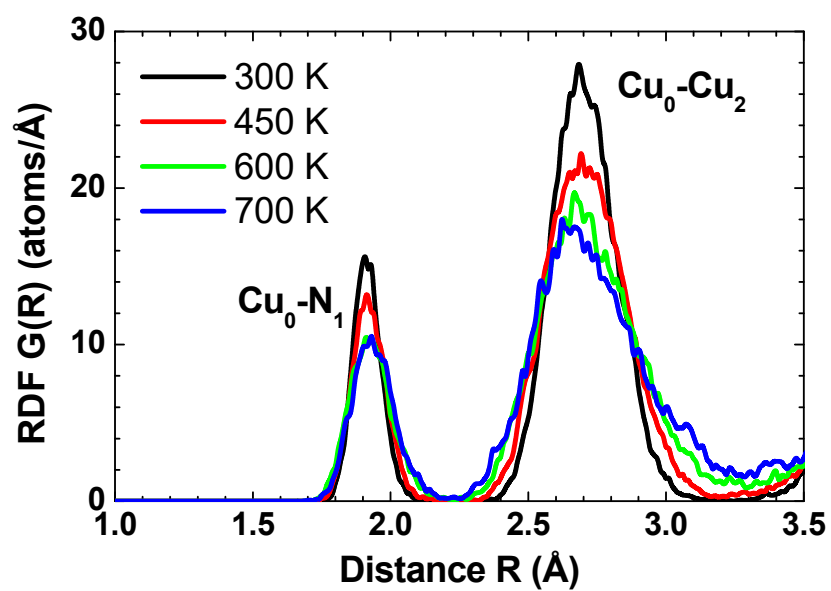


Figure 3: Temperature dependence of the radial distribution functions for Cu₀-N₁ and Cu₀-Cu₂ atom pairs obtained from AIMD simulations. Note pronounced asymmetry of both RDFs due to anharmonic lattice dynamics in Cu₃N.

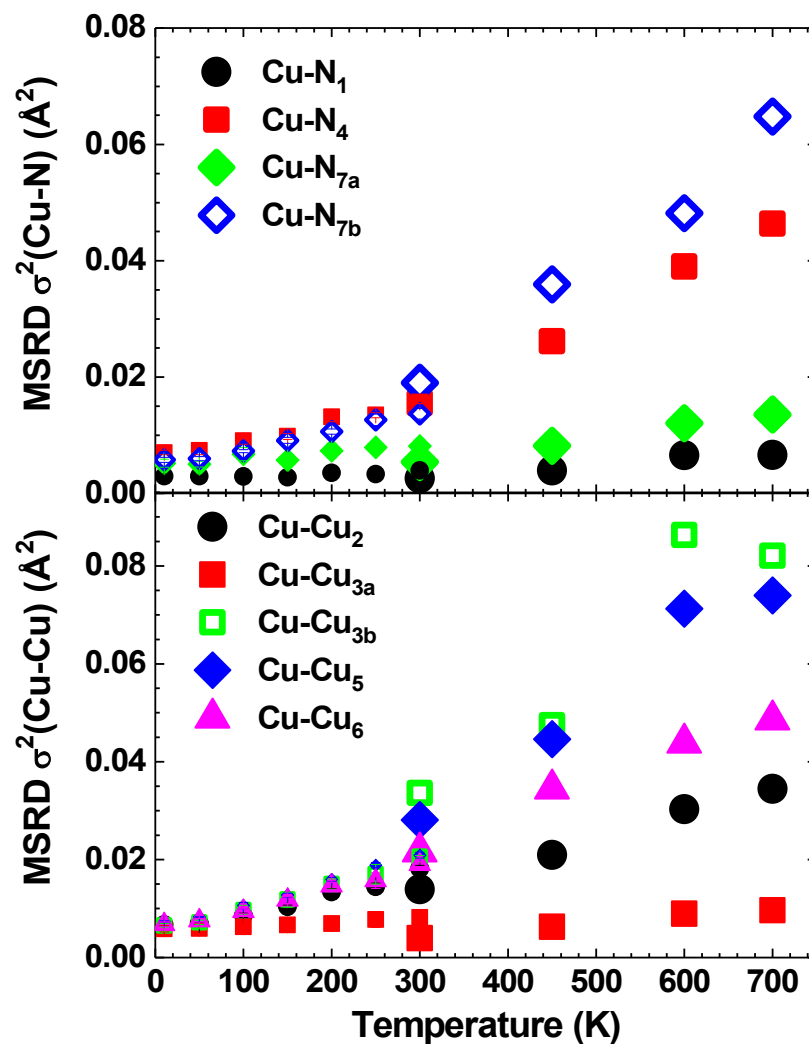


Figure 4: Temperature dependencies of the MSRD factors calculated from the results of AIMD simulations for Cu–N (top panel) and Cu–Cu (bottom panel) atom pairs in the first seven coordination shells around the absorbing (Cu₀) atoms at four different temperatures (300, 450, 600 and 700 K). The MSRD values shown by small symbols are taken from reverse Monte Carlo analysis of low-temperature (10-300 K) EXAFS data (Timoshenko et al., 2017).

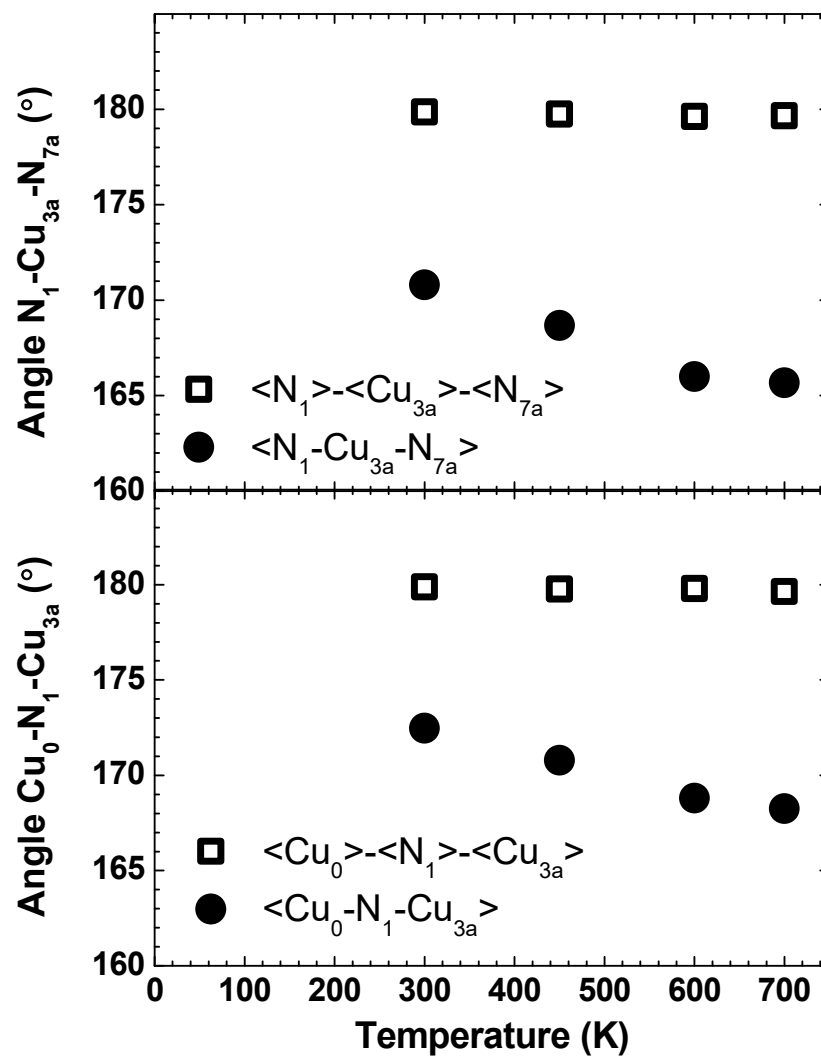


Figure 5: Temperature dependencies of the $N_1-Cu_{3a}-N_{7a}$ and $Cu_0-N_1-Cu_{3a}$ bond angle values in Cu_3N system. Open squares are angles between the average positions of atoms, whereas solid circles correspond to the average angles.

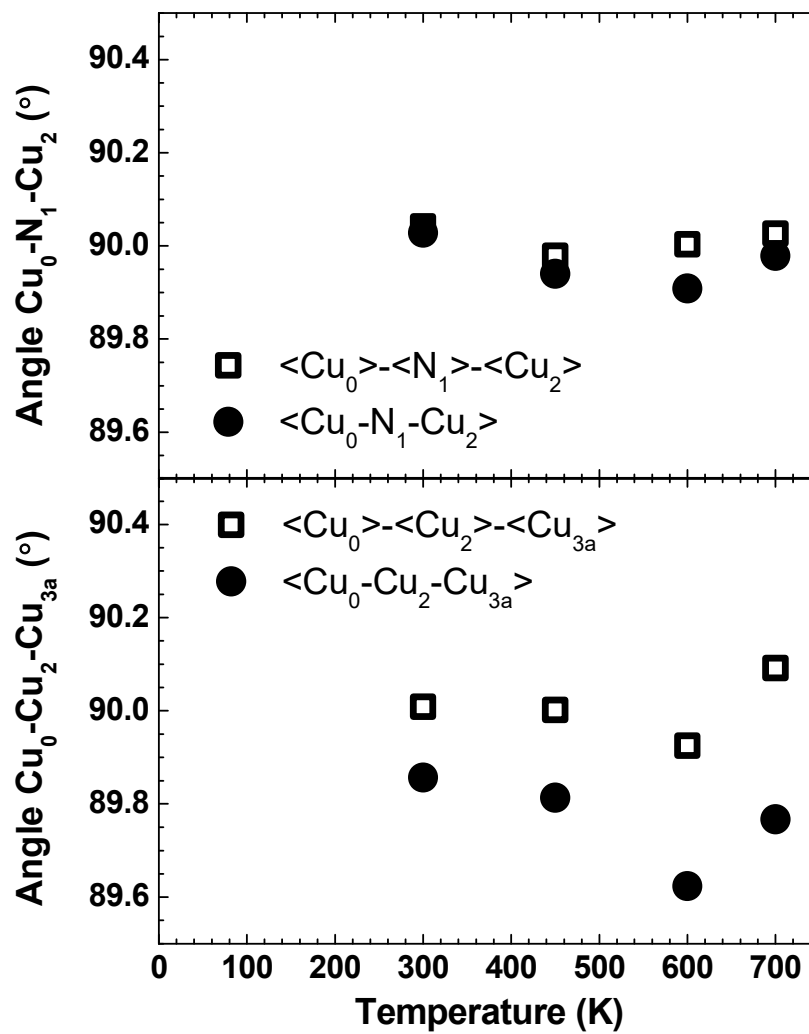


Figure 6: Temperature dependencies of the Cu₀-N₁-Cu₂ and Cu₀-Cu₂-Cu_{3a} bond angle values in Cu₃N system. Open squares are angles between the average positions of atoms, whereas solid circles correspond to the average angles.

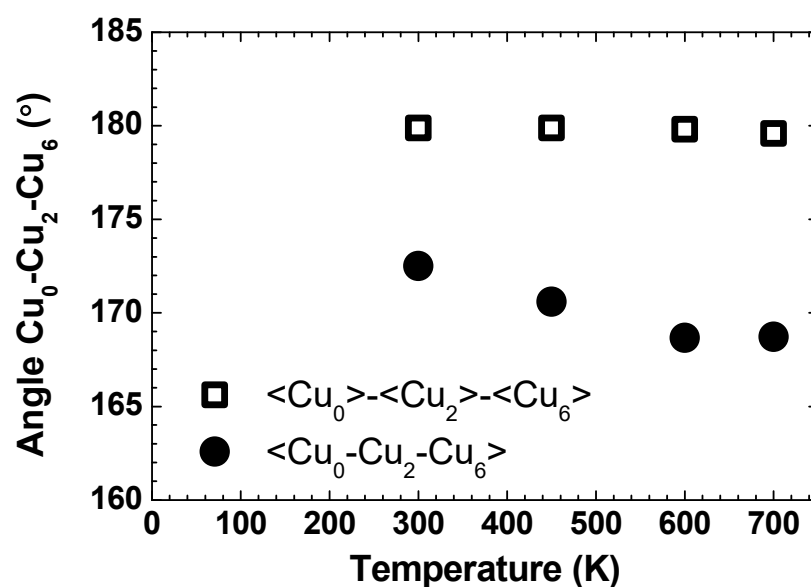


Figure 7: Temperature dependencies of the Cu₀-Cu₂-Cu₆ bond angle values in for atoms in in Cu₃N system. Open squares are angles between the average positions of atoms, whereas solid circles correspond to the average angles.

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