Local structure of copper nitride revealed by EXAFS spectroscopy and reverse Monte Carlo/evolutionary algorithm approach

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Abstract. Extended x-ray absorption fine structure (EXAFS) spectroscopy combined with reverse Monte Carlo (RMC) and evolutionary algorithm (EA) modelling is used to advance the understanding of the local structure and lattice dynamics of copper nitride (Cu_3N). RMC/EA-EXAFS method provides possibility to probe correlations in the motion of neighboring atoms and allows us to analyze the influence of anisotropic motion of copper atoms in Cu_3N .

1. Introduction

Copper nitride (Cu_3N) is a narrow band gap (0.25–1.90 eV [1]) semiconducting material with a cubic anti- ReO_3 -type structure composed of corner-shared NCu_6 octahedra [2]. It is considered as a metastable material, which loses nitrogen and turns into metallic copper upon temperature increase, and thus is a cheap and promising candidate for write-once memory devices [3, 4, 5, 6, 7]: bulk Cu_3N is stable at room temperature and decomposes at 300–450 °C, while for thin films the transition to metallic state may occur at significantly lower temperatures (down to 100 °C). Besides, copper nitride can be used in a variety of spintronics devices [8, 9], as an active layer in resistive random access memories [10, 11, 12], as a promising cathodic electrocatalyst in alkaline fuel cells [13], in optical lithography for fabrication of microscopic metal links [14, 15] and as a solar energy absorber for photovoltaic and photoelectrochemical solar cells [1, 16]. The structure of Cu_3N is compatible with the structure of some organic molecules, including porphyrins that are considered for applications in molecular-based electronics, thus this material is also interesting due its potential applications in inorganic-organic electronic devices [17]. Deep understanding of the local structure and dynamics of Cu_3N is important to fully explain and exploit its unique properties.

A peculiarity of Cu_3N lattice dynamics is significant anisotropy in the motion of copper atoms, observed by neutron diffraction [2]. One can also expect that the presence of linear $-\text{N}-\text{Cu}-\text{N}-$ atomic chains in the lattice of Cu_3N will result in significant

correlations in atomic motion, which are crucial for the description of atom dynamics in materials like ScF_3 and ReO_3 [18, 19]. Thus, despite the apparent simplicity of Cu_3N equilibrium structure, the local structure and local dynamics in this material may be far from trivial. One of a very few approaches that, nevertheless, allow one to study these issues is extended x-ray absorption fine structure (EXAFS) spectroscopy, coupled with advanced simulation-based data analysis methods. To our knowledge, in this study we apply EXAFS spectroscopy at the Cu K-edge for the investigations of Cu_3N for the first time.

EXAFS technique is a modern element-specific method to study the local atomic structure of materials [20]. The analysis of EXAFS data from the first coordination shell around the absorbing atom is based on a well-established procedure [21] and allows one to obtain distributions of distances to the nearest neighbours. At the same time, the experimental EXAFS data, acquired at modern synchrotron radiation sources, contain much more information, especially for crystalline materials. In this case, the total EXAFS consists of contributions from significantly more distant coordination shells (up to 10 Å and further). Besides, the influence of so-called multiple-scattering (MS) effects, which encode the information on many-atom distribution functions and correlations of atomic motion, is often very pronounced in cubic materials such as Cu_3N . The precise analysis of EXAFS spectra beyond the first coordination shell using conventional methods is, however, often impossible since the total number of parameters, required to completely describe the local structure, is exponentially increasing with the increase of the number of coordination shells, included in the analysis [22, 21].

To treat this issue, different simulation-based approaches can be applied: classical and ab initio molecular dynamics (MD) [23, 24, 25, 26], Monte Carlo [27] and reverse Monte Carlo (RMC) methods [28, 29]. All these approaches allow one to obtain a 3D model of material atomic structure, given by a representative set of atomic coordinates in a sufficiently large piece of investigated material. For such model the corresponding theoretical EXAFS spectrum can be calculated using existing ab initio codes [30, 31] and then compared with the experimental data. If the constructed model gives a good agreement between theoretically calculated and experimental EXAFS spectra, then one may expect that the coordinates of atoms in the model represent the atomic configuration in the real material. On the other hand, the agreement between calculated and experimental EXAFS may be used in the case of MD methods for the validation of theoretical simulations [32].

The use of ab initio MD is limited today by high computational costs of the method. Therefore, classical MD simulations are much more popular. They are based on interatomic forces that are set by empirical potentials (so-called force field models [33]). As a result, the accuracy of selected force field model limits the accuracy of the structural model. Moreover, the use of MD methods in the low temperature region, where quantum effects (zero point vibrations) give significant contribution into atomic motion, requires special treatment based on, for example, path-integral method [34]. Note that classical MD method will also fail when the character of chemical bonding in

a material changes significantly, as, for example, in semiconductor-metal transition. All these issues restrict the use of MD-EXAFS approach.

RMC simulations, in turn, do not require any additional input and do not rely, in principle, on any physical model. In this approach a 3D atomic structure of the material is reconstructed by minimizing the difference between theoretically calculated and experimental structure-related data [28]. Hence this method is quite general and can be applied to the analysis of EXAFS data for a broad range of materials and conditions. The problem of this approach, however, is that it is very time-consuming. Many thousands of iterations are required for the random process that lies at the heart of RMC method to find a structure model that is consistent with experimental data. Moreover, due to significant computational costs of *ab initio* MS EXAFS simulations for large atomic clusters, the required computational time grows exponentially with the number of coordination shells, included in the analysis. Therefore, in this study we complement the conventional RMC scheme with a powerful evolutionary algorithm (EA) for a very efficient structure model optimization. We have demonstrated recently the use of our approach on the example of perovskite-type ReO_3 [19], where the method allowed us to obtain unique information on the local structure, atomic dynamics and correlations in atomic motion in pure and hydrogen intercalated oxide.

In this study we apply RMC/EA-EXAFS approach to the investigations of polycrystalline Cu_3N with anti- ReO_3 structure. The accuracy of the results, obtained by RMC/EA approach, is validated using MD simulations.

2. Experimental details

Polycrystalline Cu_3N (99.5% purity) powder was purchased from AlfaAesar and characterized by x-ray diffraction to confirm its single phase composition. The Cu_3N powder was deposited on Millipore filter and fixed by Scotch tape for x-ray absorption measurements. The sample thickness x was optimized to obtain the Cu K-edge jump equal to $\Delta\mu x \approx 1$.

X-ray absorption measurements were performed at the Cu K-edge (8979 eV) in transmission mode at the HASYLAB/DESY C bending-magnet beamline [35] at room temperature. The storage ring DORIS III operated at $E = 4.44$ GeV and $I_{\text{max}} = 140$ mA. The higher order harmonics were reduced by detuning of the double-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 experimental Cu K-edge EXAFS spectrum $\chi(k)k^2$ was extracted using conventional procedure [36, 37] and is shown together with its Fourier transform (FT) in Figure 1. Note that contributions from atoms located up to 9 Å from absorbing copper are visible in the FT spectrum. The first two large FT peaks at ~ 1.5 Å and ~ 2.5 Å are mostly due to the single-scattering (SS) contributions from the first (Cu–N) and second (Cu–Cu) coordination shells of copper, respectively. In principle, they can be

Figure 1. (Color online) Experimental Cu K-edge EXAFS spectrum and its Fourier transform (FT) at room temperature. A fragment of crystal structure of cubic Cu_3N is shown in the inset [2].

analysed using conventional EXAFS fitting approaches [21, 36]. Further FT peaks are due to a complex superposition of SS contributions from outer coordination shells and all MS contributions, which are expected to be important in perovskite-type structure due to the presence of linear atomic chains [38]. In fact, peaks at about 3.5 Å and 5 Å are mostly due to the multiple-scattering contributions within NCu_6 octahedra and within --N--Cu--N-- linear chains. The analysis of these contributions using conventional approaches would be a challenging problem.

3. Reverse Monte Carlo/evolutionary algorithm simulations

To treat experimental Cu K-edge EXAFS data we employ an enhanced RMC-type approach, based on the use of evolutionary algorithm [19]. The combined RMC/EA scheme allows us to perform accurate analysis of EXAFS data from distant coordination shells of crystalline materials, taking into account static and thermal disorder as well as MS effects. As in the conventional RMC method, the 3D structure model of a material in our approach is optimized via the consequent proposal of random changes of atomic coordinates, and the agreement between the experimental and configuration-averaged EXAFS spectra, calculated for the proposed structure model, is used as the only criterion for the acceptance or rejection of proposed move. This configuration-averaged EXAFS spectrum is obtained from ab initio MS calculations, performed at each iteration by the FEFF8 code [30].

Implementation of the evolutionary algorithm significantly improves the convergence of the RMC optimization scheme and reduces the number of required iterations. In this case we use not just one, but several (32 in this study) structure models of the material simultaneously. The information exchange between the simulated structure models allows us to explore the configurational space more efficiently and thus the opti-

mal solution – the average atomic configuration that gives the best possible description of experimental data – is found much faster [19].

For RMC/EA calculations an initial structure model should be provided. We started with the equilibrium structure, known from diffraction experiment [2], with some small random shift for all atoms applied, and used $4 \times 4 \times 4$ supercell, containing 256 atoms, with periodic boundary conditions. The value of lattice constant a_0 was taken from diffraction studies, and was not refined during the simulations.

At each RMC/EA iteration the theoretical EXAFS spectra are calculated for each absorbing Cu atom in the supercell using ab initio self-consistent real-space MS FEFF8 code [30], taking into account MS contributions with up to eight backscatters involved. Then the configuration-averaged EXAFS spectrum is obtained. The calculation of the cluster potential is performed only once (at the beginning of simulations) for the mean crystallographic Cu_3N structure [2], thus neglecting its small variation due to thermal disorder. The complex exchange-correlation Hedin–Lundqvist potential and default values of muffin-tin radii as provided within the FEFF8 code [30] are employed.

The obtained configuration-averaged EXAFS spectrum is compared with the experimental one. Instead of comparing them directly in k -space or in Fourier transform R -space, we apply the Morlet wavelet transform [39, 40] for both spectra

$$w(k, R) = \sqrt{R/R_0} \int_{-\infty}^{+\infty} \chi(k') \varphi((R/R_0)(k' - k)) dk', \quad (1)$$

where $\chi(k)$ is the corresponding EXAFS spectrum, $\varphi(k) = \exp(-2iR_0k) \exp(-\sigma_0^2 k^2)$ is so-called mother wavelet function with the parameters R_0 and σ_0 that can improve the resolution of the transform in k -space by reducing the resolution in R -space, and vice versa. A significant advantage of using wavelet transform for EXAFS analysis is that it accounts for and shows the behaviour of EXAFS signal simultaneously in k - and R -space, thus stabilizing the solution obtained during the simulation/fit. Besides, wavelet transform allows one to discriminate between contributions of different atoms, since it is known, for instance, that light elements contribute more strongly at lower k -values than heavier elements. Indeed, contributions of Cu–N and Cu–Cu pairs are clearly separated in wavelet transform image in Figure 2.

A difference between the model and RMC EXAFS spectra can be calculated as

$$\xi_{k,R} = \frac{\|w_{\text{tot}}(k, R) - w_{\text{exp}}(k, R)\|_2}{\|w_{\text{exp}}(k, R)\|_2}, \quad (2)$$

where w_{tot} and w_{exp} are the wavelet images of the calculated and experimental EXAFS spectra, respectively, and $\|\dots\|_2$ denotes the Euclidean norm [19]. Here wavelet transforms and norm of their difference were calculated in k -space range from $3.0 \text{ \AA}^{-1}$ to $17 \text{ \AA}^{-1}$ and in R -space range from $R_{\text{min}} = 1.0 \text{ \AA}$ to $R_{\text{max}} = 6.0 \text{ \AA}$ (see Figure 2). Mother wavelet functions parameters were $\sigma_0 = 1.0 \text{ \AA}$ and $R_0 = (R_{\text{min}} + R_{\text{max}})/2$.

$\xi_{k,R}$ thus allows us to quantify the fitness of each of 32 simulated atomic configurations. By applying evolutionary operators and random atomic displacements to all atoms in all supercells, as described in [19], at each iteration from the previous

Figure 2. (Color online) Comparison of experimental Cu K-edge EXAFS and the theoretical EXAFS, obtained in RMC/EA simulations: their Fourier filtered EXAFS and Fourier transforms (upper panels) and Morlet wavelet transforms (bottom panels).

generation of atomic configurations one obtains a new set of 32 configurations, for which the difference between theoretical and experimental EXAFS spectra will, on average, be lower than for the former generation. By repeating this process a good agreement between both spectra can be obtained after several hundreds of iterations. At this moment the simulated atomic configurations will resemble the positions of atoms in the real sample. In more details the used RMC/EA scheme is presented in our recent paper [19].

The results of such simulations for room temperature Cu K-edge EXAFS in Cu_3N are shown in Figures 2 and 3. In Figure 2 the experimental EXAFS is compared with the calculated EXAFS for the final atomic configuration, obtained in RMC/EA simulation and shown in Figure 3 (left panel). One can ascertain that the structure model, obtained using RMC/EA approach, is in a good agreement with the experimental data. Also our model – stoichiometric, defect-free crystal – does not contradict to the available experimental EXAFS data, i.e., there is no evidence of Cu_3N decomposition or metallization.

From a set of atomic coordinates, obtained in RMC/EA simulation, one can calculate partial radial distribution functions (RDFs) $g(R)$ for the Cu–N and Cu–Cu atom pairs, as shown in Figure 3 (right panel) and, in principle, estimate structural

Figure 3. (Color online) Final Cu_3N structure model, obtained in RMC/EA simulations for experimental Cu K-edge EXAFS data, and corresponding partial radial distribution functions (RDFs) around copper atoms.

parameters such as average interatomic distances (RDF peak positions), distance variations (so-called mean-square radial displacement factors (MSRDs) characterizing the widths of RDF peaks), bonding angles distributions, etc. for any coordination shell with the radius smaller than the half-length of the used supercell. It is obvious that the accuracy of structural parameter values for the nearest coordination shells will be higher than for distant coordination shells. The contribution of the nearest shells into the total EXAFS spectrum is much larger, and imprecision in the average interatomic distances or relative displacements for the nearest shells would result in a significant discrepancy between experimental and calculated EXAFS. The set of structural parameters that can be reliably estimated from the results of RMC/EA-EXAFS simulations and their accuracy will be different for different materials and different absorption edges. For instance, the presence of strong MS contribution improves sensitivity of our approach to bonding angles, while the presence of heavy backscatter in the system allows one to probe more distant coordination shells. Therefore, before using the result of RMC/EA simulations for the analysis of distant coordination shells, it is important to validate that RMC/EA approach provides sufficient sensitivity for such analysis. For this purpose the RMC/EA simulations for model EXAFS data, i.e., for EXAFS spectrum, for which the corresponding structure is known in advance, can be helpful. To generate such model data, we employ here classical molecular dynamics simulations.

4. Molecular dynamics simulations

To our knowledge, no force-field models exist for Cu_3N in the literature. The development of a force field model, which would give an accurate description of local structure of the material, is a complex task and deserves a separate study. In our case, however, our intent is to use MD simulations just to validate RMC/EA procedure. Therefore we do not strive here for a precise result, and to set interatomic forces in Cu_3N we use a simple potential model close to that employed by us earlier in MD-

Table 1. Buckingham potential parameters for the Cu–N and Cu–Cu atom pairs used in molecular dynamics simulations.

Pair of atoms	A (eV)	ρ (Å)	C (eVÅ ⁶)
Cu–N	78.53	0.6241	0.0
Cu–Cu	6262	0.2525	0.0

Table 2. Covalent-exponential potential parameters for the Cu–N and Cu–Cu atom pairs used in molecular dynamics simulations.

Pair of atoms	D (eV)	a (Å ^{−1})	r_0 (Å)
Cu–N	4.378	5.231	1.910
Cu–Cu	2.375	3.473	2.700

EXAFS study of ReO_3 [41]. Our interaction potential consists of the Buckingham and covalent-exponential potentials [42]. Additionally, the Coulomb interactions were accounted using the effective ion charges $+0.5e$ for copper and $-1.5e$ for nitrogen atoms in agreement with ab initio calculations of electronic structure of Cu_3N [43]. The parameters of the Buckingham potential and covalent-exponential potential were optimized to reproduce as close as possible the lattice constant, bulk modulus and phonon frequencies of Cu_3N . Optimized values of the Buckingham potential are given in Table 1, while the values of the covalent exponential potential are given in Table 2. Note that parameter C for Buckingham potential was found to be 0 in our force field model, hence it also may be called Born-Mayer potential [44].

Classical molecular dynamics (MD) simulations were performed using the GULP code [33, 42] in the canonical (NVT) ensemble with periodic boundary conditions. The simulation box had a size of the $5a_0 \times 5a_0 \times 5a_0$ supercell including 500 atoms. Nosé-Hoover thermostat [45] was used to keep the required average temperature during each simulation. The Newton’s equations of motion were integrated using the Verlet leapfrog algorithm [46] with a time step of 0.5 fs. The equilibration and production times were 20 ps each. 4000 atomic configurations, accumulated during each production run, were then used to calculate configuration-averaged EXAFS spectrum, using the same approach as used for EXAFS calculations during RMC/EA simulations. Thus obtained model EXAFS spectrum (MD-EXAFS) is shown in Figure 4 together with its Fourier and wavelet transforms.

Next, we used the MD-EXAFS spectrum as an input for RMC/EA simulations with the same parameters and fitting ranges as used previously for the analysis of the experimental EXAFS data. The Cu K-edge EXAFS spectrum corresponding to final configuration, obtained in RMC/EA simulations for model data, is shown in Figure 4. The agreement between MD-EXAFS and RMC/EA-EXAFS data is good, indicating that RMC/EA method was able to find a structure model, consistent with the model EXAFS data. Note that there is small discrepancy between the model data

Figure 4. (Color online) Comparison of model Cu K-edge EXAFS spectrum, obtained in MD simulations, and the result of its RMC/EA reconstruction: Fourier filtered EXAFS spectra and their Fourier transforms (upper panels) and Morlet wavelet transforms (bottom panels).

and RMC/EA-EXAFS spectrum in the first coordination shell: the amplitude of the first peak in FT is lower for RMC/EA result. As will be commented below, it is an evidence that RMC/EA approach overestimates slightly the structural disorder in this case. Note that similar discrepancies between the model EXAFS data and the result of RMC/EA simulations were obtained also for RMC/EA fitting of the experimental Cu K-edge EXAFS spectrum of Cu_3N (Figure 3).

Comparison of structural parameters, obtained from RMC/EA modelling for the model EXAFS data, with their known values allows one to estimate the uncertainties of the analysis also for the experimental data.

5. Results and discussion

Structural parameters of the MD model are compared with the results of RMC/EA reconstruction for the first 16 coordination shells around copper in Figure 5. Each point in the graphs corresponds to a specific coordination shell, and we show separately structural parameters for pairs of atoms that are located within a single —N—Cu—N— chain and for atom pairs located off this chain. Here we focus on two types of parameters: (i) MSRD factors, which characterize the variation in the interatomic distances due to atom

Figure 5. (Color online) Comparison of structural parameters of MD model (..MD) with the results of RMC/EA reconstruction (..RMC/EA): relative average interatomic distances with respect to crystallographic values $\Delta R = R - R_{\text{eq}}$ (see equation (3)) and MSD factors for the first 16 coordination shells.

motion in the direction of interatomic bond and (ii) a difference ΔR between the average interatomic distance R and the distance R_{eq} between the average positions of atoms. Note that due to the motion of atoms in the direction, perpendicular to interatomic bond, average interatomic distances R , measured by EXAFS, are always larger than crystallographic distances R_{eq} between the average positions of atoms [47]. Hence $\Delta R = R - R_{\text{eq}}$ can be used to characterize the amplitude $\langle u_{\perp}^2 \rangle$ of atomic displacement in the direction perpendicular to interatomic bond [47]. It is known, in fact, that average interatomic distance R , as probed by EXAFS, and perpendicular MSD factor $\langle u_{\perp}^2 \rangle$ are related by equation [47]

$$R \approx R_{\text{eq}} + \frac{\langle u_{\perp}^2 \rangle}{2R_{\text{eq}}}. \quad (3)$$

RMC/EA method provides values slightly larger than those for the original MD structure both for MSD and ΔR (Figure 5). This finding is consistent with the observation that RMC-type methods tend to converge of all possible structure models that agree with experimental data to the one that have the maximal disorder. For all coordination shells the difference between values of ΔR parameters, obtained in RMC/EA simulations, and true values for MD model is smaller than 0.005 Å. It may seem surprising that the largest differences are observed in the values of ΔR for the first coordination shell, which gives the most significant contribution to the EXAFS spectrum. This finding, however, is in agreement with Equation (3): overestimation in disorder in the direction, orthogonal to interatomic bonds, will affect more the lengths of short bonds. The longer bonds are less affected by the disorder effects, and accuracy of their lengths determination is closely related to the accuracy of lattice constants values, used for RMC/EA simulations.

The differences between the values of MSD factors, obtained in RMC/EA simulations, and the values for MD model are smaller than 0.001 Å² for two nearest

Table 3. Structural parameters (MSD factors and Cu–N–Cu angle φ) for MD model and for final configuration, obtained in RMC/EA simulations of model data. See details in text.

Parameter	MD	RMC/EA for MD
$\text{MSD}^{11}(\text{N}) = \text{MSD}^{22}(\text{N}) = \text{MSD}^{33}(\text{N})$ ($\text{\AA}^2$)	0.00458	0.0045(1)
$\text{MSD}^{11}(\text{Cu})$ ($\text{\AA}^2$)	0.00288	0.0034(4)
$\text{MSD}^{22}(\text{Cu}) = \text{MSD}^{33}(\text{Cu})$ ($\text{\AA}^2$)	0.00106	0.010(1)
φ ($^\circ$)	173.0	170.9(3)

coordination shells and for Cu–Cu pairs, located within the –N–Cu–N– chain: these groups of atoms contribute strongly to the total EXAFS spectrum, hence our analysis is quite sensitive to them. Systematic errors of MSD factors for other coordination shells may be several times larger, since the values of MSD factors themselves are large, which results in reduced amplitudes of corresponding contributions to the total EXAFS spectrum. Note here that small values of relative displacements of atoms in the nearest coordination shells are ensured by correlations in atom motion, which, naturally, decrease with the increase of corresponding interatomic distance.

Note that the test results, presented here, allow one to estimate systematic errors of RMC/EA fitting procedure only, and do not account, for instance, for systematic errors due to EXAFS extraction procedure, sample homogeneity issues, monochromator stability, etc. Also imprecisions due to inaccuracies of FEFF calculations were not taken into account here, since the same FEFF theory [30] was used both for generation of MD-EXAFS model data and for RMC/EA reconstruction. It is believed that FEFF based analysis of experimental EXAFS data provides interatomic distances with accuracy about 0.01 $\text{\AA}$, thus systematic errors, introduced by RMC/EA procedure, are still smaller than the ones, introduced by the use of current FEFF theory.

Besides MSDs and interatomic distances, there are several additional important structural parameters. Mean square displacement (MSD) factors characterize the absolute deviations of atoms from their equilibrium positions. These quantities are usually obtained from diffraction experiments, but simulation-based EXAFS analysis can also be used for this purpose: indirect information about MSD factors is encoded in angular dependencies of MS contributions and in contributions of distant coordination shells [48], where the motion of atoms is almost uncorrelated, hence their MSD factors can be expressed just as a sum of corresponding MSDs. These quantities are summarized in Table 3. Motion of nitrogen atoms in Cu_3N is isotropic, hence their MSD values along –Cu–N–Cu– chain direction and in two orthogonal directions (denoted further as $\text{MSD}^{11}(\text{N})$, $\text{MSD}^{22}(\text{N})$ and $\text{MSD}^{33}(\text{N})$) are equal. This MSD value is estimated reliably in the structure model, obtained in RMC/EA calculations for model MD-EXAFS data: the value of $\text{MSD}^{11}(\text{N}) = \text{MSD}^{22}(\text{N}) = \text{MSD}^{33}(\text{N})$ agrees with the result of RMC/EA simulation within error bars. The motion of copper atoms is significantly anisotropic,

Table 4. Structural parameters for Cu_3N , obtained by RMC/EA analysis of experimental room temperature EXAFS data and in diffraction experiments.

Parameter	RMC/EA	Diffraction [2]	Diffraction [49]
$\text{MSD}^{11}(\text{N}) = \text{MSD}^{22}(\text{N}) = \text{MSD}^{33}(\text{N})$ ($\text{\AA}^2$)	0.006(1)	0.0058(1)	0.0060(8)
$\text{MSD}^{11}(\text{Cu})$ ($\text{\AA}^2$)	0.008(1)	0.00246(6)	0.0048(6)
$\text{MSD}^{22}(\text{Cu}) = \text{MSD}^{33}(\text{Cu})$ ($\text{\AA}^2$)	0.017(2)	0.0124(4)	0.012(1)
φ ($^\circ$)	169.9(3)	-	-

and $\text{MSD}^{11}(\text{Cu})$ factor, corresponding to their motion along $-\text{Cu}-\text{N}-\text{Cu}-$ chain direction, is significantly smaller than $\text{MSD}^{22}(\text{Cu})$ and $\text{MSD}^{33}(\text{Cu})$ factors. This anisotropy is well reproduced by our RMC/EA method. Note, however, that $\text{MSD}^{11}(\text{Cu})$ value is slightly overestimated.

Finally, another important parameter is the angle φ between neighboring $\text{N}-\text{Cu}$ and $\text{Cu}-\text{N}$ bonds in $-\text{N}-\text{Cu}-\text{N}-$ chain (i.e., the tilting angle of NCu_6 octahedra). For equilibrium structure of Cu_3N this angle is equal to 180° . Due to thermal motion of atoms, however, locally the average value of this angle is always smaller, and will be the smaller, the larger are displacements of Cu atoms in the direction orthogonal to the $-\text{N}-\text{Cu}-\text{N}-$ chain. The value of φ , obtained in RMC/EA simulations, is about 2° smaller than the one for the MD model, indicating once again that the disorder of Cu_3N is slightly overestimated in RMC/EA simulations.

Further we will discuss the results, obtained by RMC/EA method for the experimental Cu K-edge EXAFS data for Cu_3N , measured at room temperature.

Variations of ΔR and MSRD factors for different Cu-Cu and Cu-N pairs as a function of corresponding crystallographic distance R_{eq} are shown in Figure 6, while the obtained values of MSD factors and average φ angle are given in Table 4. MSD factors, obtained by our RMC/EA-EXAFS analysis, are compared here with the results of neutron diffraction studies [2]. MSD values for nitrogen, obtained by two methods, agree within error bars, and also significant anisotropy of copper atom vibrations is clearly evidenced by both methods. Our analysis, however, suggests significantly larger values of MSD both in the direction of $-\text{N}-\text{Cu}-\text{N}-$ chain and in the orthogonal directions. Note that the difference between copper MSD values, obtained by our EXAFS analysis and by neutron diffraction, exceeds significantly the uncertainty of our method, estimated in our study of model EXAFS data, and would require a separate investigation in the future.

In Figure 6 (right panel) we compare MSRD factors for the Cu-N bond with the sum of corresponding MSD factors for copper and nitrogen atoms. Note that the knowledge of MSRD and MSD factors for the two atoms A and B allows one to estimate correlation effects: $\text{MSRD}(\text{A}, \text{B}) = \text{MSD}(\text{A}) + \text{MSD}(\text{B}) - 2\text{cov}(\text{A}, \text{B})$, where $\text{cov}(\text{A}, \text{B})$ is the covariance of displacements of atoms A and B and accounts for correlation in atom motion [20].

Figure 6. (Color online) Results of the analysis of the experimental Cu K-edge EXAFS data: relative interatomic distances with respect to crystallographic values $\Delta R = R - R_{\text{eq}}$ (see equation (3)) and MSRD factors for different Cu–Cu and Cu–N pairs as functions of corresponding crystallographic distance R_{eq} . Dashed lines in the right panel – sum of corresponding copper and nitrogen MSD factors (as copper MSD the averaged value of $\text{MSD}^{11}(\text{Cu})$, $\text{MSD}^{22}(\text{Cu})$ and $\text{MSD}^{33}(\text{Cu})$ is used).

It is instructive to examine MSRD values for atom pairs located within single linear –N–Cu–N– chain and to compare them with MSRDs for atoms in the off-chain positions. Note that the MSRD factors for atom pairs located along a single chain are relatively small. Striking examples of the difference between off-chain and in-chain MSRDs can be seen in the 3rd and 7th coordination shells of copper atoms ($R_{\text{eq}} = 3.850 \text{ \AA}$ and $R_{\text{eq}} = 5.775 \text{ \AA}$, correspondingly, as highlighted in Figure 6 (right panel)). Note that there are six copper atoms in the 3rd coordination shell of each copper. While all these six copper atoms have the same equilibrium distance to central copper, two of them are located within a –N–Cu–N– chain with the absorbing copper atom, while the remaining four are located in the off-chain positions. Despite the fact that R_{eq} value is the same for all six copper atoms in the 3rd coordination shell, the MSRD factors for these two groups of atoms are significantly different. Similar findings can be done for the 7th coordination shell, consisting of two nitrogen atoms in the in-chain positions and eight nitrogen atoms in the off-chain positions.

Differences of MSRDs for in-chain and off-chain atoms can be a result of smaller amplitudes of copper oscillations in the direction along the chain, as well as due to differences in the correlations of atom motion for in-chain and off-chain pairs. Taking into account that the MSRDs for off-chain pairs are close to the sum of corresponding MSDs for copper and nitrogen atoms and show weak dependence on interatomic distance, while the MSRDs for in-chain pairs grow with the increase of interatomic distance, one can conclude that the correlation of atom motion in the direction of –N–Cu–N– chain plays an important role for dynamics of in-chain atoms. Such directional dependence of atomic interactions in Cu_3N suggests the presence of pronounced covalent bonding in this material, as predicted by ab initio studies of its electronic structure [43].

Figure 7. (Color online) Results of the analysis of the experimental Cu K-edge EXAFS data: distribution of Cu–N interatomic distances in the first coordination shell around Cu atoms and bonding angle distribution function (BADF) of N–Cu–N angles φ . The latter is defined as probability density $h(\varphi)$ to encounter angle with value φ , divided by $\sin(\varphi)$. For comparison, the results for ReO_3 [19] are also shown.

Note also that such behaviour of the MSRD factors is similar to the one, observed by us for crystalline ReO_3 [50]. For more detailed analysis of interatomic interactions in Cu_3N temperature-dependent EXAFS studies of Cu_3N should be carried out.

Note that we do not observe any significant differences in the behavior of ΔR parameters within the precision of our analysis for in-chain and off-chain atom pairs (Figure 6 (left panel)). In both cases the dependencies of ΔR parameter are in a qualitative agreement with Equation (3). This result suggests that there are no significant correlations in the atom motion in the direction orthogonal to $-\text{N}-\text{Cu}-\text{N}-$ chain direction.

Finally, let us discuss our results regarding the angle between neighbouring NCu_6 octahedra. Its value has been a subject of controversy in the literature [2, 49]. Our results indicate that the cubic structure of Cu_3N (where the angle between octahedra, formed by equilibrium positions of Cu and N atoms, as seen by diffraction studies [2], is 180°) is fully consistent with the experimental EXAFS data. At the same time, the average N–Cu–N angle φ is smaller than 180° due to oscillations of copper atoms in the directions, orthogonal to $-\text{N}-\text{Cu}-\text{N}-$ chains. In fact, our results suggest that this effect is very pronounced in Cu_3N . The obtained distribution of N–Cu–N bonding angles is shown in Figure 7, and, when compared with the corresponding distribution for Re–O–Re angles in ReO_3 [19], one can conclude that it is much broader in Cu_3N . Hence the average N–Cu–N angle value ($\sim 170^\circ$) is significantly smaller than that in ReO_3 ($\sim 174^\circ$), indicating the presence of large anharmonic vibrations of copper in Cu_3N . Tentatively they can be attributed to the tilting motion of NCu_6 octahedra, since the relatively small value of MSRD factor for the shortest Cu–N bond implies rigidity of NCu_6 unit. Note that it is pointed out in [51], from electronic structure point of view it should

be easier to tilt the NCu_6 octahedra in Cu_3N than ReO_6 octahedra in ReO_3 , and our results support this finding. Such strong anharmonic motion of copper atoms should result in non-Gaussian shape of the RDF for the first coordination shell (Cu–N bond), and, indeed, it is clearly seen in our results, obtained by RMC/EA method (Figure 7 (left panel)).

6. Conclusions

In this paper we report on the first EXAFS study of the local structure in polycrystalline Cu_3N at room temperature. The experimental Cu K-edge EXAFS data were analysed by advanced simulation-based method, involving the use of reverse Monte Carlo, evolutionary algorithm and wavelet transform approaches. We have demonstrated that the RMC/EA-EXAFS method is sensitive enough to analyze the local structure of Cu_3N within up to 8 Å from absorbing copper atom. It was found that the dynamics of copper atoms is essentially anisotropic, in agreement with previous neutron diffraction studies [2], and the Cu–N bonding is significantly covalent, as predicted by theoretical investigations [43]. Additionally, we have demonstrated that (i) motion of copper atom is strongly anharmonic and (ii) correlation effects play important role in the dynamics of neighboring atoms.

Acknowledgments

The work was supported by Latvian Science Council Grant No. 187/2012. The EXAFS experiments at HASYLAB/DESY were supported by the EC FP7 under grant agreement No. 226716 (Project I-20110160 EC).

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