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Thermal disorder and correlation effects in anti-perovskite-type copper nitride

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ABSTRACT

Reverse Monte Carlo simulations coupled with evolutionary algorithm were employed for the analysis of the temperature dependent (10–300 K) Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra of polycrystalline copper nitride (Cu_3N) with the goal to extract information on the thermal disorder and interatomic correlations in anti-perovskite-type crystal lattice. The obtained results are discussed in comparison with metallic copper and perovskite-type rhenium trioxide. The analysis of EXAFS spectra suggests that the anisotropy of copper atom vibrations is significantly enhanced upon increasing temperature, leading to pronounced tilting motion of NCu_6 octahedra. Strong correlation in the motion of atoms was found along –N–Cu–N– atomic chains but it reduces rapidly with an increase of interatomic distance. Finally, anticorrelated motion of neighboring Cu atoms occurs along Cu–Cu bonds and is consistent with breathing-type motion of NCu_6 octahedra.

1. Introduction

Materials with perovskite-type structure are appealing due to their relatively simple and stable structure, numerous possible technological applications and a broad range of properties, which can be tuned, e.g., by substituting cations at the sites A and B of ABX_3 perovskite crystal lattice [1–6]. Many of the unique properties of perovskite-type materials are a result of local distortions and peculiar atomic dynamics in such materials. Importance of such effects as anisotropy and anharmonicity of atomic vibrations and the presence of strong correlations in atomic displacements is acknowledged, for instance, in many studies of phase-transitions [7–9], ferroelectric properties [7,10,11] and negative thermal expansion effect [12–15], observed in perovskites.

So-called anti-perovskite materials have similar to perovskites crystal structure, which can be described by the same formula ABX_3, but now the X site is occupied by a metal cation, while B site is occupied by light anion. While less studied than perovskites, anti-perovskite-type materials also exhibit a number of intriguing properties, such as giant negative thermal expansion, observed in Ge-doped MnN [16], superconductivity, observed in $MgCNi_3$ [17], and giant magnetoresistance, detected for Mn_3GaC [18]. One can expect that the local structure and dynamics play as important role for the understanding of properties of anti-perovskites as they do in the case of perovskites. Nevertheless, the dynamical properties and interatomic correlations in anti-perovskites have been investigated to much less extent.

Therefore in this study we apply a novel approach, which combines possibilities, provided by X-ray absorption spectroscopy and advanced simulation-based analysis, to investigate the local structure and dynamics of copper nitride Cu_3N, a narrow band gap (0.25–1.90 eV [19]) semiconductor with a cubic anti-perovskite-type structure. Particular attention is paid to the analysis of interatomic correlations and their dependence on temperature.

Copper nitride consists of regular, corner-shared NCu_6 octahedra [20,21] (see the inset in Fig. 1), and is a metastable material. Cu_3N thin films can be easily produced by magnetron sputtering, and their crystallinity can be controlled by substrate temperature [22]. Upon temperature increase above 100 °C nitrogen is released from thin film Cu_3N, and the material turns into metallic copper. Hence the use of copper nitride in write-once memory devices [23–27], as a seed layer for electrodeposition [28] and in optical lithography for fabrication of metal links [29,30] was proposed. At the same time, bulk material is stable at room temperature, but

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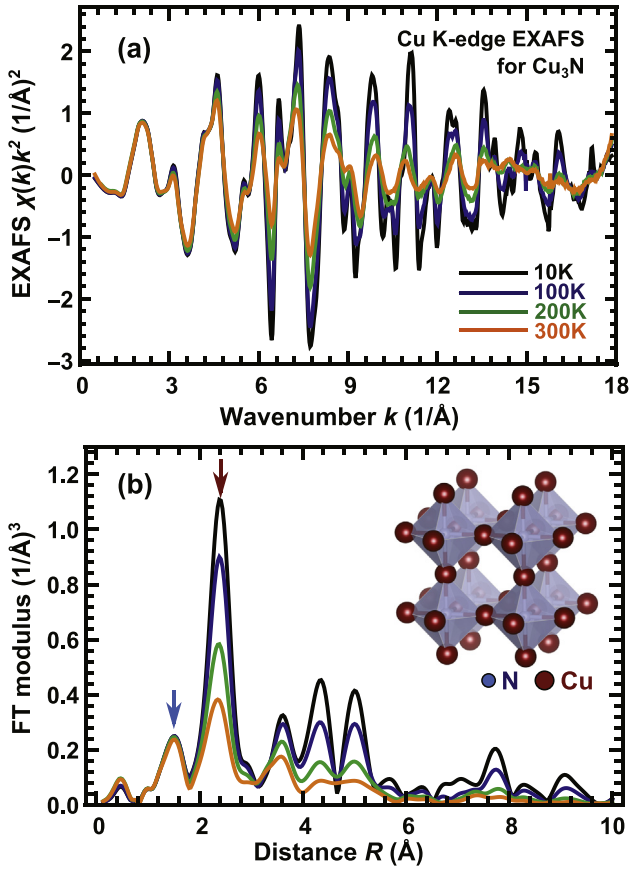

Fig. 1. The experimental Cu K-edge EXAFS spectra (a) and their Fourier transforms (FTs) (b) at four selected temperatures. The first peak at 1.3 Å corresponds to two nearest nitrogen atoms of the first coordination shell of copper, whereas the second peak at 2.4 Å corresponds to eight copper atoms forming the second coordination shell. The inset in (b) shows the crystal structure of cubic Cu_3N composed of NCu_6 octahedra [20,21].

decomposes at 300–450 °C. Other possible applications of Cu_3N are related to spintronics [31,32], electrocatalysis [33], solar energy conversion [19,34], resistive switching memories [35,36] and inorganic-organic electronics [37].

The equilibrium structure of Cu_3N is known from X-ray [20] and neutron [21] diffraction. The results obtained by both methods show also a significant anisotropy of copper thermal motion, which increases upon temperature increase [20]. In this sense the behaviour of Cu_3N is similar to the one, observed for such perovskite-type materials as rhenium oxide ReO_3 and scandium fluoride ScF_3 [14,15,38]. The character of chemical bonding in Cu_3N, in turn, has been a subject of the discussion in the literature. In particular, theoretical studies suggest covalent bonding of Cu and N atoms rather than simple ionic interaction between Cu^{1+} and N^{3-} ions [39]. At the same time, it was proposed in Ref. [40] that metallic-type bonding may also contribute to the properties of Cu_3N, especially at elevated pressures. Note that copper-copper distances in Cu_3N are just slightly larger than those in close-packed metallic copper [41,42]. Together with the fact that Cu_3N is easily transforming into metallic copper upon temperature increase, this observation may allow to speculate that interatomic interactions in Cu_3N may resemble those in copper. Experimental evidences on the character of such interactions, however, currently are absent.

To investigate this issue, we employ advanced analysis of the Cu K-edge extended X-ray absorption fine structure (EXAFS). EXAFS spectroscopy is a well-established experimental technique to study the distributions of interatomic distances within the nearest coordination shells around absorbing atom. During the last decades it was widely used to study the local structure and dynamics in a broad range of materials [43–45]. The possibilities to use EXAFS data to probe interatomic correlations, in turn, are much less exploited, despite the fact that sensitivity of EXAFS to these effects is acknowledged [45–47].

We have demonstrated recently [48,49] that it is feasible to obtain the information on interatomic correlations, if EXAFS analysis is coupled with theoretical simulations and such advanced approaches as reverse Monte Carlo (RMC) [50] and evolutionary algorithm (EA) [48] methods. The combined RMC/EA-EXAFS approach was successfully applied to studies of such perovskite-type materials as ReO_3, H_xReO_3 [48,49,51,52], $SrTiO_3$ [53] and FeF_3 [54].

In this study we apply RMC/EA-EXAFS method to extract information on interatomic distances and amplitudes of absolute and relative atomic motion within the first seven coordination shells around Cu atoms in Cu_3N. Note that the validation of RMC/EA-EXAFS approach for Cu_3N was presented in Ref. [55]. Here we analyze temperature dependent changes in the structural parameters upon temperature increase from 10 K to 300 K. The central result of this paper is the analysis of correlations in the motion of nearest Cu–N and Cu–Cu neighbors. We show that despite the fact that the crystallographic structure or ReO_3 and Cu_3N are the same, correlation properties are very different in these two materials.

2. Experimental details

Temperature-dependent Cu K-edge (8979 eV) X-ray absorption spectra of Cu_3N were acquired in transmission mode at the bending magnet beamline C [56] at HASYLAB/DESY synchrotron radiation facility. For this experiment we used commercially available polycrystalline Cu_3N powder (99.5% purity), purchased from Alfa Aesar. The powder was characterized by X-ray diffraction to confirm its phase purity.

To achieve the best homogeneity of the sample for XAS measurements, polycrystalline Cu_3N powder was deposited on Millipore filter, and then fixed by Scotch tape. The sample thickness x was optimized to obtain the jump in X-ray absorption coefficient at the Cu K-edge equal to $\Delta\mu_x \approx 1$.

During the XAS measurements, the storage ring DORIS III operated at the energy $E = 4.44$ GeV and with the current $I_{max} = 140$ mA. Double crystal Si(111) monochromator was used for energy selection. To remove the higher order harmonics, the crystals were detuned by 60%. For this purpose the beam-stabilization feedback control was employed. The intensity of X-ray beam before and after the sample was measured using ionization chambers, filled with argon and krypton gases. Copper foil was used as a reference material for energy calibration. Its room temperature Cu K-edge X-ray absorption spectrum was simultaneously acquired and used later for data alignment. The temperature of the sample was controlled in the range from 10 K to 300 K using helium-flow cryostat.

The experimental Cu K-edge EXAFS spectra $\chi(k)k^2$, acquired at different temperatures, were extracted, aligned and processed using conventional procedure [57,58]. They are shown together with their Fourier transforms (FTs) in Fig. 1.

Low temperature Cu K-edge X-ray absorption spectra of copper foil at $T = 10$ and 150 K, which were used for comparison, were taken from Ref. [59].