

## Phase transition of bismuth nanoparticles

H. Ikemoto<sup>1</sup>, H. Maekawa<sup>1</sup>, H. Isono<sup>1</sup>, K. Hatada<sup>1</sup>, and T. Miyanaga<sup>2</sup>

<sup>1</sup> Department of Physics, University of Toyama, Toyama 930-8555, Japan

<sup>2</sup> Department of Advanced Physics, Hirosaki University, Hirosaki 036-8561, Japan

ikemoto@sci.u-toyama.ac.jp

Bismuth is characterized by a hierarchical structure: Bi atoms are arranged in a sheet structure by the equivalent three-folded covalent bonds, and the sheets are stacked in stable form, which is known as A7 type structure. In the fifth group elements Arsenic and Antimony make the same structure as Bi. Phosphorous also makes a similar structure, but because there are two types of covalent bonds, is called A17 type structure. Bi is an important element in view of its presence in many studied topological materials. In this presentation, we report a study on the local structure of Bi nanoparticles (n-Bi). In particular, we discuss the phase transition from A7 to A17 type structure in n-Bi.

Samples of n-Bi were synthesized using the island deposition method. We measured XAFS spectra of the pellets of Bi and NaCl multilayers at BL-12C of the Photon Factory (PF) in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan.

In the Fourier transform of XAFS functions the first peak around 3.0 Å, which is originated from the covalent bond, appears clearly. However, the second peak around 3.6 Å, which is originated from the interlayer nearest neighbor, dumps largely compared with that of the crystalline Bi (c-Bi). This suggests that the primary structure which is made by the covalent bonds remains even in n-Bi, but the interlayer interaction weakens largely.

At first the Fourier filtered XAFS function corresponding to the covalent bond were analyzed with the model of the A7 type structure, that is, assuming just one type of covalent bond. The covalent bond length is 3.05 Å, which is equivalent with that of c-Bi. However, the coordination number is about two, which means the Bi atoms form ring or chain structures, not the sheet structure typical of the crystalline Bi. The value of the covalent bond length may contradict the coordination number, because the change of the structure usually causes the change of the covalent bond length.

Next, we analyzed them with the A17 type structure getting a hint from the phosphorous stable form. In this analysis the two types of the covalent bond were assumed with the coordination number fixed at one and two and the Debye-Waller factors fixed at the values of c-Bi obtained by the analysis on the A7 type structure model. In c-Bi the covalent bond lengths of the two types are the same within the error. However, in n-Bi the values of the covalent bond lengths are 3.03 and 3.17 Å. It is reasonable to assume that there are two types of covalent bonds in the n-Bi, which implies that the Bi sheets transform from the pyramidal (A7) to the chair (A17) in n-Bi.

The difference between c-Bi and n-Bi appears also in the XANES spectra. Theoretical calculations are in progress using FPMS code which has advantages for anisotropic structures.

In n-Bi there would be two types of the covalent bonds, and the primary structure would transform from the pyramidal (A7) to the chair (A17) structure.

The synchrotron radiation experiments were performed at the Photon Factory in KEK under Proposal No. 2006G304, 2008G509, 2010G612, and 2014G573.