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Modulated Structure of η'-Cu_{3+x}(Si,Ge) Determined by Quantitative Electron Diffraction Tomography

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Despite its technological importance *e.g.* as a catalyst for the production of highly important chlorosilanes [1], η'-$Cu_{3+x}Si$ has eluded correct structural description for decades due to the combination of a complex, two-dimensional incommensurately modulated structure, and difficulty to obtain large samples suitable for single crystal analysis. All previous studies involved powder samples [2], thin films on a substrate [3], or precipitates in a silicon substrate [4].

Small isolated platelets about 40 nanometres thick with composition η'-$Cu_{76.1}Si_{11.7}Ge_{12.2}$ were obtained by deposition of organometallic precursors (hexamethyldigermane $Ge_2(CH_3)_6$ and ethyl silane $SiH_3C_2H_5$) on Cu substrate by the CVD method at temperature of 500 °C.

Initial investigation of the samples was performed on a JEOL JEM-3010 transmission electron microscope with LaB_6 cathode operating at 300kV. First, oriented diffraction patterns of several platelets were collected (Fig. 1a). These patterns revealed an incommensurately modulated structure. The complex diffraction pattern is not a consequence of twinning, but it stems from one phase. This is evidenced by high-resolution TEM images (Fig. 1b,c). The data for structural investigation were collected by quantitative electron diffraction tomography coupled with precession electron diffraction on a Philips CM120 with LaB_6 cathode operating at 120kV equipped with a precession device SpinningStar (NanoMegas). The structure was solved by the charge-flipping algorithm in superspace [5].

The structure is trigonal, and it is incommensurately modulated with two modulation vectors $q_1 = (\alpha,\alpha,1/3)$ and $q_2 = (-2\alpha,\alpha,1/3)$, superspace group $P\ \bar{3}1m$ $(\alpha,\alpha,1/3)000(-2\alpha,\alpha,1/3)000$. η'-$Cu_{3+x}$(Si,Ge) has a layered structure with layers stacked along c. One unit cell contains of the average structure contains six layers. Only four of these six layers are symmetry independent (Fig. 2). The structure could be also envisioned as slabs of Cu clusters separated by monoatomic layers of Si and Ge atoms (Fig. 3). The Cu slabs are strongly modulated, leading to a predominant icosahedral coordination of the central Cu atoms. The two-dimensional modulation functions describing the shifts of the atoms show an unprecedented complexity and large amplitude. The conflict between the strive for locally favorable icosahedral coordination of the Cu atoms and the need for a long-period arrangement is the most likely reason for the modulation.

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[6] This research was supported by the Grant Agency of the Czech Republic (No. 203/09/1088).

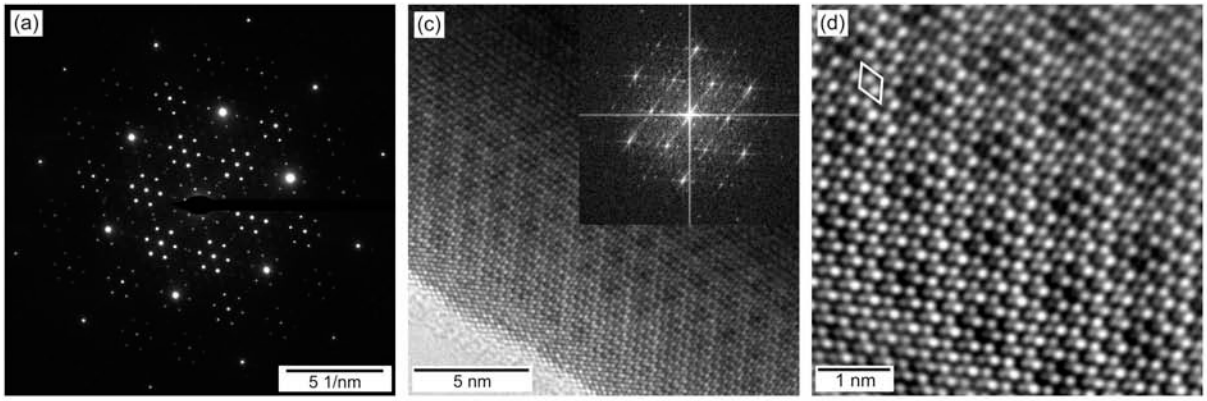

FIG. 1. TEM observations. (a) Diffraction pattern of the zone [001]. (b) HRTEM image. (c) A Fourier-filtered scale-up of (c) showing clearly the non-periodic variation of the contrast. The basic unit cell is shown by the white rhombus.

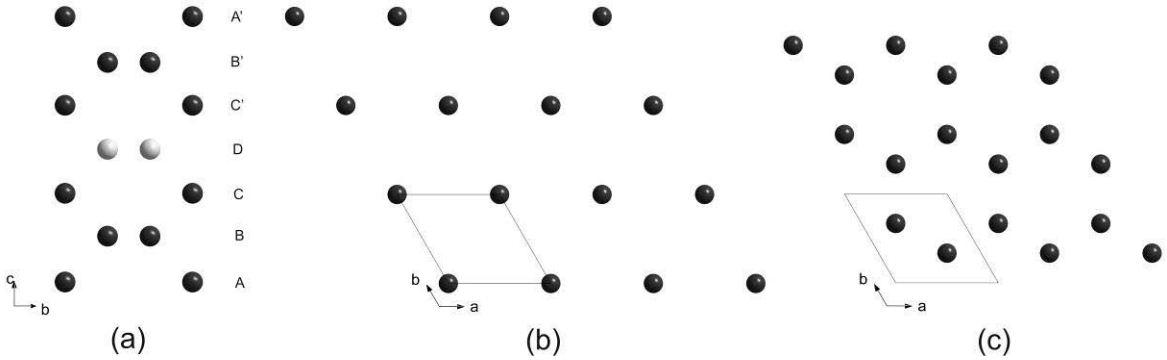

FIG. 2. Average structure of η'-Cu_3(Si,Ge). (a) View along [100]. Dark spheres represent Cu, light spheres are Si-Ge mixed sites. Layers labeled with different letters are symmetry independent, primed labels denote layers related by inversion center. (b) Distribution of atoms in close-packed layers A and C. (c) Distribution of atoms in honey-comb layers B and D.

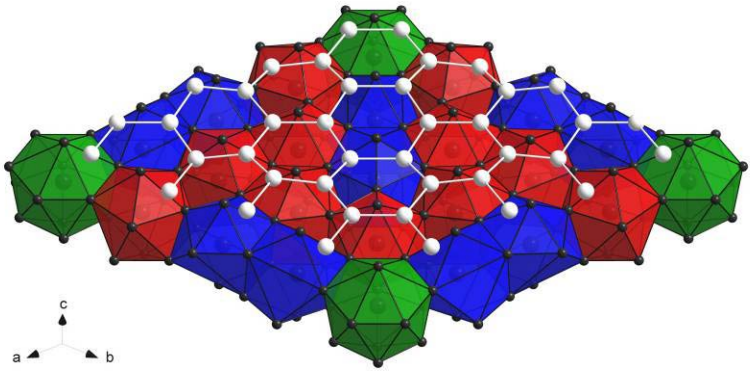

FIG. 3. Structure in the 4x4 supercell approximation showing one slab of Cu clusters and one layer of Si/Ge atoms. Different colors distinguish different coordinations of the central Cu atoms in the slab.

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