

Surface step structure of $\text{Ag}_{13}\text{OsO}_6$, experimental evidence for Ag_{13} cluster building blocks

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The surface of single crystal $\text{Ag}_{13}\text{OsO}_6$ has been investigated using atomic force microscopy. Growth spirals with very large flat terraces, separated by steps of equal height, have been observed. The measured step height of $\sim 6.7 \text{ \AA}$ corresponds to the diameter of one Ag_{13} -icosahedron and identifies the cluster as the key structural building block.

A macroscopic crystal is composed of a very large number of atoms that respond collectively to integral chemical or physical probes. Thus, it is generally difficult to assign a particular structural, bonding or physical motive to subsets of the constituting elements. Nevertheless, for the sake of comprehension and classification, this has been done with ample success.

In this approach, however, a certain degree of arbitrariness is involved. One can represent a microporous solid by graphically emphasizing selected polyhedra and their connectivities, or create clusters by drawing direct homoatomic connections, in spite of the fact that these atoms are held together by bridging ligands. In this context, lines can have many different meanings, varying from "guides to the eye" to "chemical bonds". It is obvious that independent probes are needed to make such assignments less ambiguous. Here we demonstrate that imaging of crystal surface structures by atomic force microscopy (AFM) can be a useful tool to identify cluster units as the structural motif.

Based on structural considerations we have proposed recently that $\text{Ag}_{13}\text{OsO}_6$ is built of Ag_{13} -clusters (centred icosahedron) and OsO_6 -anions.¹ This interpretation seemed justified since the intra-cluster bonds to the central atom of the icosahedron are shortest (2.79 Å). However, the next longest bonds are not those in the deltahedral surface of the icosahedron, but those to the six adjacent clusters. Taking these latter distances into account one would end up with a "void metal", instead of "isolated" clusters.

We focus here on the surface morphology of $\text{Ag}_{13}\text{OsO}_6$ crystals. By using AFM we have been able to obtain detailed insights into the surface morphology and growth mechanism. We find that the crystal grows in rectangular spirals with very large flat terraces, with adjacent terraces being separated by steps of a height corresponding to half the unit cell of $\text{Ag}_{13}\text{OsO}_6$. The latter is taken as direct evidence for the presence of Ag_{13} clusters.

Crystals of $\text{Ag}_{13}\text{OsO}_6$ were grown by a reaction of ground mixtures of silver and osmium metal powders at elevated oxygen pressure in a steel autoclave.^{1,2} To prepare single crystals, 1 ml of H_2O was added as a mineraliser. In the autoclave we also inserted a silver disc (1 cm in diameter; 1 mm in thickness) and found that crystals nucleated on the disc as well as in the crucible. The crystals obtained from the crucible are silvery with a metallic lustre and cubic shape showing an edge length of typically 100 μm (see Fig. 1a). The crystals grown on the silver disc are somewhat smaller showing an edge length of approximately 10 μm (see Fig. 1b). We believe that the smaller size of crystals grown on the Ag plate is due to the enhanced nucleation density leading to a limitation in size of the individual crystals.

No further cleaning after the synthesis of the crystals was performed before AFM imaging. The surface of single crystal $\text{Ag}_{13}\text{OsO}_6$ has been investigated with AFM ("Nanoscope IIIa" from DI) under ambient conditions. The AFM was operated in "tapping mode", where the cantilever is oscillating allowing the tip to briefly touch the surface at the maximum of each oscillation

period. The AFM height measurement has been calibrated by scanning the surface of etched mica, which has a known step height of 1 nm.³ In Fig. 2a, a typical AFM image of the $\text{Ag}_{13}\text{OsO}_6$ surface is shown where terraces and steps can clearly be identified. The lateral extension of the terraces varies somewhat from crystal to crystal, and we have observed sizes of 0.1 to 1 μm in one direction and much longer (up to 10 μm) in the other direction. The steps are very long and straight without any kinks or other defects. Only corners of 90° are present on the surface and we observe that the crystals are growing in rectangular spirals. Although the presence of kinks should be favored for entropic reasons we observe here that the creation of kinks must be energetically disfavoured. Note that the observed average terrace width of 120 nm in Fig. 2a results in a macroscopic crystal surface, which differs by only 0.3° from a perfect flat surface. This is comparable to the flatness of low index metal single crystal surfaces of the highest quality. Step edges are oriented along the macroscopic directions of the crystals and the microscopic growth thus reflects the overall shape of the crystals. We further note that the crystals shown in Fig. 1b all have the same orientation. We did not observe any difference at the surface of crystals grown on a silver plate or the ones grown in the crucible.

A closer look at the surface is presented in the AFM image shown in Fig. 2b. We note some noisy appearance of the terraces, which is believed to be due to the presence of adsorbate impurities since experiments were performed under ambient conditions. The height difference between adjacent terraces is very well resolved and has been determined to be $(6.7 \pm 0.5) \text{ \AA}$ as indicated by the linescan across the surface (see Fig. 2c). This is a rather large value in comparison with pristine metal single crystals. The observed step height was identical on all samples investigated.

The measured step height corresponds perfectly to half the unit cell of $\text{Ag}_{13}\text{OsO}_6$, which is approximately 13.2 Å. Due to the alternating orientation of the icosahedra in the crystal (see Fig. 3) the step height also corresponds to the diameter of the individual Ag_{13} cluster. The AFM measurement thus clearly identifies the cluster as building block of the crystal structure. In comparison to

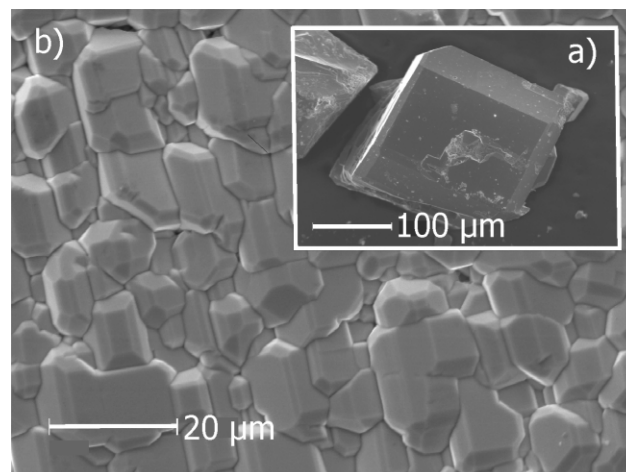


Fig. 1 Typical SEM images of $\text{Ag}_{13}\text{OsO}_6$ crystals. a) crystal grown in a gold crucible, b) crystals grown on the surface of a silver disc.

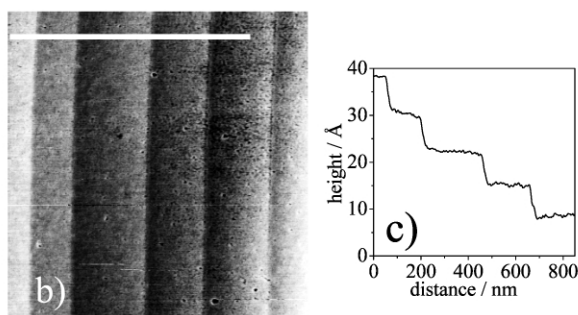
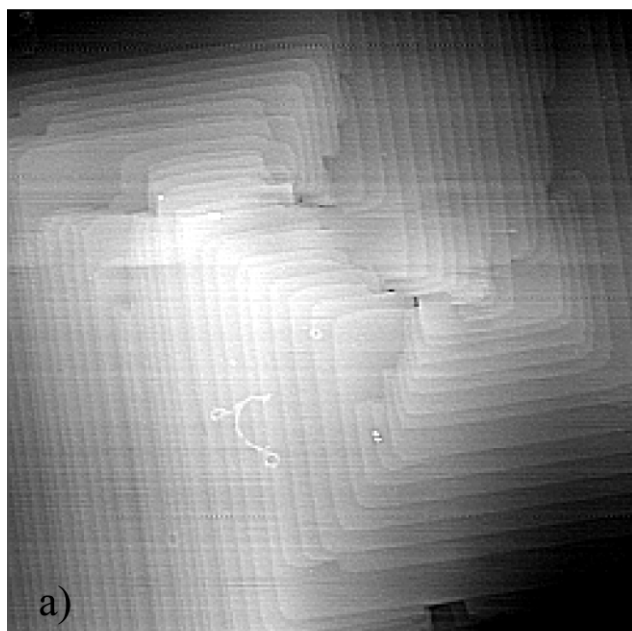


Fig. 2 a) AFM Image of $\text{Ag}_{13}\text{OsO}_6$ surface, image size $(6.6 \mu\text{m})^2$, b) Smaller area $(1.0 \mu\text{m})^2$ c) linescan (white line in b)) showing the step-height of $\sim 6.7 \text{ \AA}$ between adjacent terraces. The sample shown in b) is slightly tilted. This tilt has been removed in the linescan in c) for clarity.

pure single crystal Ag, where exclusively monatomic steps are observed, the present data show that the intra-cluster Ag–Ag bonds in the Ag icosahedron are apparently stronger than the inter-cluster bonds.

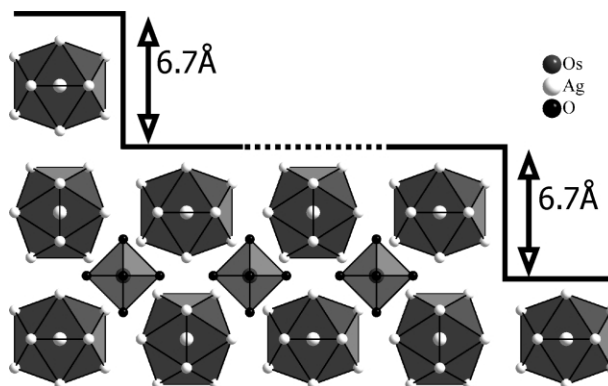


Fig. 3 Correlation between the measured step height and crystal structure. The dashed line indicates a large terrace width ($\sim 120 \text{ nm}$) and the solid vertical line represents the step height. Drawn are Ag_{13} icosahedra and OsO_6 octahedra.

This is corroborated by recent theoretical LMTO calculations.¹ It was found that the 12 intra-cluster bonds from the central Ag atom have a bond strength of 0.65 eV, *i.e.* are significantly stronger than the two types of inter-cluster bonds, which have a bond strength of only 0.41 eV and 0.60 eV, respectively. We therefore believe that the Ag-icosahedra are the structural building blocks and the step structure corresponds to the situation depicted in Fig. 3. Although alternating terraces originate from different parts of the unit cell, the surface composition of each terrace is the same, since the larger unit cell is due to the rotated Ag_{13} clusters.

Notes and references

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