[Contribution from the Department of Chemistry, McGill University]

SINGLE CRYSTALS OF SILVER

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A large number of metallic single crystals have been prepared. Hauser[1] has obtained symmetrical etch figures on spherical single crystals of copper and silver which show the crystallographic form of the metal. Various other workers have obtained rods or wires which consisted of one crystal. As far as we are aware, however, large single metallic crystals possessing the characteristic external form have not been previously prepared.

Experimental

During the course of another investigation[2] some very pure silver was prepared. The method of preparation was to dissolve silver nitrate in water and allow the solution to settle. Silver chloride was precipitated from the filtered solution by the addition of hydrochloric acid. It was then reduced to the metal by boiling with invert sugar and sodium hydroxide. The precipitate was thoroughly washed with hot distilled water and fused to a button in a crucible under borax. Analysis of the purified silver showed 0.003% of copper, 0.001% of lead and a trace of iron.

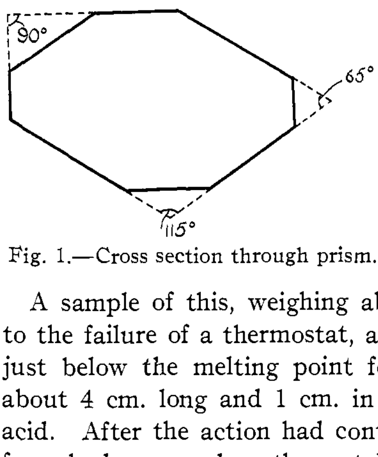

Fig. 1.—Cross section through prism.

A sample of this, weighing about 30 g., was accidentally fused owing to the failure of a thermostat, and was then cooled very slowly and kept just below the melting point for several days. The ingot, which was about 4 cm. long and 1 cm. in diameter, was treated with dilute nitric acid. After the action had continued for some time it was noticed that faces had appeared on the metal, and on examination it was found to be an octagonal prism weighing about 7 g. The crystal form is described later.

Apparently the original bar of silver consisted of a single crystal and the acid attacked the different faces in a specific manner, finally yielding an octagonal prism.

The fact that a well-defined crystal was obtained was undoubtedly due to the high degree of purity of the silver, which prevented any local electrolytic action such as would take place if impurities were present.

Hauser's crystals, prepared similarly by slow cooling, were turned into spheres on a lathe and then etched superficially with acids. The crystal-

[1] Hauser, *Ber. Siemens Konzern,* **1927.**

[2] *Proc. Roy. Soc., London,* **117A,** 662 (1928).

line form was inferred from the shape of the resulting etch figures; in no case was the external form characteristic of the crystal obtained.

The preparation of crystals in this manner was repeated. Twenty grams of silver was placed in a quartz bulb in an electric furnace. The silver was melted and thoroughly evacuated to prevent spitting on solidification. It was necessary to shake the bulb during evacuation in order to prevent small bubbles of gas from sticking to the walls below the surface of the silver and causing irregularities in the ingot. The metal was then slowly cooled (about 5° per hour) and kept at a temperature of 940° for forty-eight hours. On treating with dilute nitric acid a crystal similar to the previous one, weighing about 4 g., was obtained.

In order to prepare satisfactory crystals it is necessary that the cooling should be slow and preferably from the bottom of the tube in order to avoid a pit at the surface. The presence of oxygen must be avoided.

We are indebted to Dr. R. P. D. Graham, Professor of Mineralogy at McGill University, who kindly examined the crystals and reported as follows.

"The two crystals examined are prismatic in habit. Each has a diameter of about $^1/_4$ inch, and they are, respectively, $^7/_8$ inch and $^5/_8$ inch in length.

"On both, there are eight faces in the prism zone, and some of them are surprisingly flat, although none are sufficiently so to yield images on the reflecting goniometer. Other faces are somewhat concave and irregularly pitted.

"The longer crystal is terminated at one end by four ill-defined planes of the latter type, which form a pyramid whose apex is replaced by a tiny smooth face at right angles to the prism. The relation of these terminal faces to the eight faces of the prism zone is such as to suggest that the crystal is a combination of cube and dodecahedron elongated in the direction of a cubic axis. If such is the case, however, the crystal is highly distorted, as the angle between adjacent faces in the prism zone is not 45°, as it should be if they represent faces of the cube and dodecahedron.

"Of these faces in the prism zone, four, taken alternately, are inclined to one another at 90°, and assuming the four terminal faces to be faces of the dodecahedron, these four prism faces also belong to the dodecahedron.

"The remaining four faces in the prism zone are symmetrically disposed with regard to the first set, and together they would form a prism having an angle of about 65°. If, therefore, they are faces of the cube, the crystal is much distorted. There is nothing, however, to indicate that the crystals are twinned. It is possible that the faces represent the development of two pairs of faces belonging to a four-faced cube (tetrahexahedron). The angle $hk0:kh0$ for the four-faced cube (510) is 67° 23′, and for the form (410) it is 61° 55$^3/_4$′. The latter form has been observed on crystals of native silver."

Summary

Single crystals of silver can be prepared by slow cooling of the molten metal. Dilute acid attacks the faces in a specific manner, yielding prismatic crystals.

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