# The external shape of antimony oxide (Sb$_2$O$_3$) formed on the cleavage surface of stibnite.

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By means of electron diffraction, Miyake (1938) has established the following facts on the growth of antimony oxide (Sb$_2$O$_3$) upon the cleavage surface of stibnite (Sb$_2$O$_3$): (i) the [110] axis of the oxide is parallel to the [001] axis of the stibnite; and (ii) the oxide grows into a protrusion having an external shape bounded by two well developed octahedral planes (111) and (11$\bar{1}$), and by less developed planes (1$\bar{1}$1) and (1$\bar{1}$$\bar{1}$), as shown in Fig. 1.

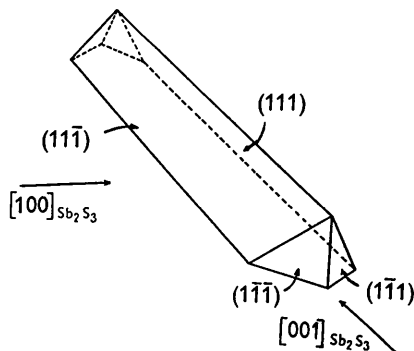The latter conclusion was deduced from the study of the fine structure in the electron-diffraction pattern,



Fig. 1. The external shape of the antimony oxide deduced from electron diffraction (Miyake, 1938).

taking account of the refraction at the boundary surfaces and the external shape. It seemed interesting to confirm this conclusion directly by means of electron microscopy.

A fresh cleavage surface of stibnite was oxidized by heating in air at 280° C. for 20 min., which is, according to Miyake, the most favourable condition for this form of growth of the oxide. The oxidized surface was investigated by the replica method. A step replica (Wyckoff 1949), utilizing a solution of 1·5% nitrocellulose dissolved in amylacetate, was found to be the best. The electron micrograph obtained is reproduced in Fig. 2.

It clearly shows roof-like oxide protrusions of dimen-

sions about 2–4 $\mu$ (length) and 0·1–1 $\mu$ (width) in relief against the flat substrate and growing nearly parallel to



Fig. 2. The electron micrograph of the roof-like oxide formed on the cleavage surface of the stibnite.

one another. This agrees well with the conclusion mentioned above. As far as our electron micrograph is concerned, however, the shape of the oxide protrusion does not seem so clean-cut as indicated in Fig. 1, showing that the top edge of the roof is somewhat round. This rounding cannot be due to the lack of faithfulness in the replica, since we can find the well defined edge at the bottom of the protrusion.

### References

MIYAKE, S. (1938). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **34**, 565.

WYCKOFF, R. W. G. (1949). *Electron Microscopy.* New York: Interscience Publishers.

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# An incorrect expression in the literature for the electron density in a crystal.

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The electron density at any point in the unit cell of a crystal is given, in the usual notation, by the Fourier series

$$\varrho(x, y, z) =$$

$$\frac{1}{V} \sum_{h}^{+\infty} \sum_{k} \sum_{l} F_{hkl} \cos \{2\pi(hx/a + ky/b + lz/c) - \delta_{hkl}\} . \quad (1)$$

James (1948) and Bragg (1929) quote, in addition to (1), the expression

$$\varrho(x, y, z) =$$

$$\sum_{h} \sum_{k} \sum_{l} A_{hkl} \cos\left(2\pi \frac{hx}{a} - \delta_h\right) \cos\left(2\pi \frac{ky}{b} - \delta_k\right) \cos\left(2\pi \frac{lz}{c} - \delta_l\right),$$

$$(2)$$

in which axes $a$, $b$ and $c$ are not in general rectangular. Neither James nor Bragg uses (2) but each develops (1) without apparently realising that, in general, (1) and (2) are not identically equal but only become so for certain

combinations of symmetry elements. Each term in (2) gives sinusoidal variations of density in directions parallel to the three axes only, whereas each term in (1) gives sinusoidal variations in all directions.

Expression (2) was originally given by Epstein & Ehrenfest (1924); Compton (1926) correlated $A_{hkl}$ with $F_{hkl}/V$.

Duane (1925) showed that for sodium chloride $\delta_h = \delta_k = \delta_l = 0$, since sodium chloride crystals possess three mutually perpendicular mirror planes. For such a crystal expression (2) reduces to

$$\varrho(x, y, z) =$$
$$\frac{1}{V} \sum_h^{+\infty} \sum_k \sum_l F_{hkl} \cos 2\pi\, hx/a \cos 2\pi\, ky/b \cos 2\pi\, lz/c \ . \quad (3)$$
$$_{-\infty}$$

This was the expression used by Havighurst (1925a, b, 1926, 1927) in investigating the structure of sodium chloride and other crystals. For sodium chloride $\delta_{hkl}$ also is zero and $F_{hkl} = F_{\bar{h}kl} = F_{h\bar{k}l} = F_{hk\bar{l}}$. Hence, by combination of the Fourier terms corresponding to these coefficients, expression (1) also reduces to (3) (Compton & Allison, 1935). The expression used by Duane and Havighurst was therefore correct, although derived from the incorrect form (2).

Other conditions for which (1) and (2) will reduce to a common form are possible, but arise only from certain combinations of symmetry elements which are not present in the general case.

### References

BRAGG, W. L. (1929). *Proc. Roy. Soc.* A, **123**, 537.
COMPTON, A. H. (1926). *X-rays and Electrons*, p. 151 *et seq.* London: Macmillan.
COMPTON, A. H. & ALLISON, S. K. (1935). *X-rays in Theory and Experiment*, p. 451 *et seq.* London: Macmillan.
DUANE, W. (1925). *Proc. Nat. Acad. Sci., Wash.* **11**, 489.
EPSTEIN, P. & EHRENFEST, P. S. (1924). *Proc. Nat. Acad. Sci., Wash.* **10**, 133.
HAVIGHURST, R. J. (1925a). *Proc. Nat. Acad. Sci., Wash.* **11**, 502.
HAVIGHURST, R. J. (1925b). *Proc. Nat. Acad. Sci., Wash.* **11**, 507.
HAVIGHURST, R. J. (1926). *J. Amer. Chem. Soc.* **48**, 2113.
HAVIGHURST, R. J. (1927). *Phys. Rev.* **29**, 1.
JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*, p. 344. London: Bell.

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# The orientation relationships between cementite and $\alpha$-iron. By N. J. PETCH, *Leeds University, England*

An examination of the precipitation of cementite in the tempering of martensite, which the present author hopes to publish in detail later, is relevant to the recent paper under this title by Trillat & Oketani (1952).

In martensite, the c.p. hexagonal $\varepsilon$-carbide occurs transitionally in the precipitation (Jack, 1951). The best structural fit between cementite and $\varepsilon$-carbide, and a very good one at that, is given by (001) $Fe_3C \parallel$ (112) $\varepsilon$, [100] $Fe_3C \parallel [\bar{1}10] \varepsilon$. Also, in spite of the apparent complexity of cementite, the difference between the two structures lies simply in the stacking and spacing apart of (112) $\varepsilon$ and the planes parallel to (001) $Fe_3C$. Cementite has mirror planes at $z = \pm\frac{1}{4}$ and this stacking can be obtained by a heterogeneous twinning of (112) $\varepsilon$ in the $[\bar{1}\bar{1}1]$ direction. Prismatic interstices are generated on the mirror planes and the carbon atoms migrate into these interstices (there is probably also some rejection of carbon). This accommodation of the carbon atoms does not require any displacement of the iron atoms in the same plane, but the spacing apart of the planes becomes unequal, depending upon whether or not there is carbon-iron contact between them. Thus, it appears probable that (001) $Fe_3C \parallel$ (112) $\varepsilon$ will give the cementite–$\varepsilon$-carbide orientation because of both the good structural fit and the simplicity of the structural relationship in this orientation.

$\varepsilon$-Carbide forms stringlets, whereas cementite forms platelets (Jack, 1951), so the cementite must eventually grow out of the $\varepsilon$-carbide into the iron solid solution. By that time, the precipitate may have broken away from the matrix and its growth will then be independent of the structural fit; if, however, break away has not taken

place, a slight distortion will make (001) $Fe_3C$ parallel to, and in register with, the $\alpha$-iron planes corresponding to (112) $\varepsilon$. These $\alpha$-iron planes belong to the two cubic forms {112} and {125} and the following are representative orientations:

(001) $Fe_3C \parallel$ (211) $\alpha$; [100] $Fe_3C \parallel [0\bar{1}1] \alpha$;
(001) $Fe_3C \parallel$ (2$\bar{1}$5) $\alpha$; [100] $Fe_3C \parallel [\bar{3}11] \alpha$ .

Precipitation from ferrite, instead of martensite, possibly involves $\varepsilon$-carbide, but there may be direct nucleation of cementite. In the latter case, it appears reasonable to suppose that the orientation may again be given by (001) $Fe_3C$ on {112} $\alpha$ or {125} $\alpha$ since these provide the best interfacial fits; that with {112} $\alpha$ is possibly rather the better and may be preferred.

Trillat & Oketani, in their single crystals of iron carburised at 500° C., found (111) $Fe_3C \parallel$ (001) $\alpha$, (1$\bar{2}$1) $Fe_3C \parallel$ (110) $\alpha$. These planes do not themselves represent any close structural fit, but this orientation corresponds almost exactly with the fit of (001) $Fe_3C$ on {112} $\alpha$. The occasional occurrence of the orientation (100) $Fe_3C \parallel$ (001) $\alpha$, (010) $Fe_3C \parallel$ (100) $\alpha$ was also detected and this may be due to the rather special nature of their specimens. These were thin films with (001) faces, so the second orientation possibly represents surface nucleation with (100) $Fe_3C$ fitted to (001) $\alpha$.

### References

JACK, K. H. (1951). *J. Iron Steel Inst.* **169**, 26.
TRILLAT, J. J. & OKETANI, S. (1952). *Acta Cryst.* **5**, 469.