

Short Communications

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On the existence of a h.c.p. phase in thin films of samarium metal. By C. BOULESTEIX, *Institut d'Optique, Faculté des Sciences, 91 Orsay, France*, P. E. CARO, M. GASGNIER and CH. HENRY LA BLANCHETAIS, *Laboratoire des Terres Rares, C. N. R. S., 92 Bellevue, France* and B. PARDO and L. VALIERGUE, *Institut d'Optique, Faculté des Sciences, 91 Orsay, France*.

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Electron diffraction patterns obtained with thin samarium films by Kumar & Srivastava are due to *B*-type Sm_2O_3 formed during annealing of the films and not to a new (h.c.p.) phase of samarium as they claimed.

Our studies on thin films of samarium metal by X-ray diffraction, electron microscopy and diffraction (Boulesteix, Gasgnier, Henry la Blanchetais & Valiergue, to be published) have never revealed the existence of a h.c.p. phase as recently claimed by Kumar & Srivastava (1969).

However, their results are very close to those we have obtained on oxidized thin films of samarium metal. Samarium metal takes up oxygen very readily even in a good vacuum, if heated. It is quickly oxidized to *C*-type Sm_2O_3 (body centered cubic) in a dynamic vacuum (10^{-6} torr) between 200° and 350°C. *C*-type Sm_2O_3 recrystallizes on further heating into large crystals of *B*-type Sm_2O_3 (monoclinic). The recrystallization phenomenon can be observed directly in the electron microscope under the heating of the electronic beam. The vacuum in the electron microscope being ordinarily around 10^{-5} torr, oxidation can also occur directly. The conditions used by Kumar & Srivastava (1969) to anneal their films obviously lead to oxidation.

We were able to make thin films of *B*-type Sm_2O_3 by oxidizing samarium metal. The electron diffraction patterns for the crystals of *B*- Sm_2O_3 are identical with those reported as proof of a h.c.p. structure by Kumar & Srivastava (1969). The reason for the mistake is that *B*- Sm_2O_3 has a structure which is a slight deformation of the hexagonal *A*- Ln_2O_3 (Ln = rare earth) structure, and, moreover, the crystals have a particular orientation.

The diffraction pattern presented in Fig. 2 of the paper by Kumar & Srivastava is, in fact, not hexagonal. The central spot has six close neighbour spots, but two of them are closer to the central one than the other four. The ratio of the lengths is 1.077, equal to the interplanar distance ratio of planes (202) and (111) of *B*-type Sm_2O_3 . Moreover the interplanar distances calculated, $d_{202} = 3.46 \text{ \AA}$ and $d_{111} = 3.21 \text{ \AA}$, are those of *B*-type Sm_2O_3 . It is easy to index all the diffraction spots in terms of the monoclinic unit cell. The surface of the film is parallel to the (20 $\bar{1}$) plane of the *B*-type crystal. The (20 $\bar{1}$) plane is itself parallel to the basal plane of the hexagonal $(\text{LnO})_n^{2+}$ packing of OLn_4 tetrahedra in *B*- Ln_2O_3 (Caro, 1968). The variation of 8% of the distances measured on the diffraction pattern is very much larger than the error due to the ellipticity of the electron diffraction pattern. Nevertheless the pattern was described by Kumar & Srivastava as having hexagonal symmetry.

We therefore claim that the h.c.p. structure described by Kumar & Srivastava (1969) for thin films of samarium metal is indeed monoclinic *B*-type Sm_2O_3 . A paper submitted to this journal describes our work on *B*- Sm_2O_3 thin films (Boulesteix, Caro, Gasgnier, Henry la Blanchetais & Pardo, 1970).

Our samarium metal thin films, deposited on optically polished glass, show, depending on the experimental conditions (substrate temperature and thickness) the classical rhombohedral (Ellinger & Zachariassen, 1953; Daane, Rundle, Smith & Spedding, 1954) or the double h.c.p. (Jarayaman & Sherwood, 1964) structure. Very thin films whose thickness is smaller than, or close to, 500 Å always have the rhombohedral structure. On X-ray patterns the lines 100, 211, 221 and 10 $\bar{1}$ are always present and intense whatever the experimental conditions. The line 333, characteristic of the compact basal plane appears only very infrequently. In our opinion this indicates a preferred orientation of the crystals: they have the compact plane perpendicular to the surface of the films. The films deposited on a substrate heated at a temperature lower than 200°C do not seem to be oxidized: no lines characteristic of samarium sesquioxide, either *C*-type or *B*-type, appear on the patterns.

By electron microscopy and diffraction the samarium metal thin films appear to be single-crystal in thickness for thicknesses smaller than 1000 Å. Crystals exhibit numerous twins, the twin planes being the planes (333).

References

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