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Evidence for a new phase structure of samarium. By JITENDRA KUMAR and O.N.SRIVASTAVA, *Department of Physics, Banaras Hindu University, Varanasi-5, India.*

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Thin samarium films, studied by electron diffraction techniques, exhibit a structure which does not correspond to the known rhombohedral structure of samarium. Evidence and arguments, based on diffraction analysis, are presented for the new phase being a hexagonal close-packed structure. The lattice parameters for this structure are: $a=3.65$ and $c=5.86$ Å.

Many metals are polymorphic and have more than one stable structure. Some famous examples are the α - γ modifications of iron (Taylor, 1952), face-centred cubic and hexagonal close-packed forms of cobalt (Edwards & Lipson, 1942; Taylor, 1952) and the body-centred cubic, hexagonal close-packed and face-centred cubic structures of chromium (Abrahamson & Grant, 1956).

Samarium belongs to the rare-earth metal series and is believed to have a rhombohedral structure with $a=8.982$ Å and $\alpha=23.31^\circ$. This structure was proposed by Ellinger & Zachariassen (1953) based on powder X-ray diffraction studies. Daane, Rundle, Smith & Speeding (1954) used single-crystal methods and found their intensities at variance with those reported by Ellinger & Zachariassen. They also noticed some streaking between certain reflexions which was indicative of some type of disorder. In order to explain the observed intensities Daane *et al.* used the Hendricks & Teller (1942) formalism of order-disorder between layers; these results predict a submicroscopic twinning in the crystal. Samarium, like La, Ce, Pr and Nd (Pearson, 1967), thus seems to exhibit a structure which deviates from the cubic or hexagonal close-packed arrangements.

The present investigation on samarium, employing electron diffraction and electron microscopy methods, originated with a desire to study the structural features suggested by Daane *et al.* and also to study the dislocations and deformation modes. During this work we have observed that the vacuum-deposited polycrystalline and single-crystal films exhibit a hexagonal close-packed structure. This seems to be a new phase of samarium differing from the structures suggested by Ellinger & Zachariassen and Daane *et al.*

Thin films were prepared by a method similar to that employed for the rare-earth metal gadolinium (Srivastava & Silcox, 1968). Both polycrystalline and single-crystal films of thicknesses ~ 500 Å were examined in the electron microscope.

Fig. 1 shows an electron diffraction pattern obtained from a polycrystalline samarium film. The lattice spacings corresponding to various lines were calculated in the usual way using a camera constant which had been determined with a silver film standard. A comparison of the d values with those obtained for a rhombohedral structure shows that there are several discrepancies. Many of the important lines which are to be expected from a rhombohedral structure do not appear. A survey of the arrangement of the diffraction lines and comparison of the d values with the d values of the other h.c.p. rare-earth metals suggested the possibility of a hexagonal close-packed structure. Taking the structure as close-packed with the a parameter as suggested by Daane *et al.* and assuming the c/a ratio to be ideal, *i.e.* $=1.63$ (which is approximately true for the h.c.p. rare-earth metals), we find that the indices of the lines are consistent with those expected from an h.c.p. structure. The indices of the lines are indicated in Fig. 1.

In order to verify the above conjecture, the diffraction analysis was extended to single-crystal films. It is known (see Srivastava & Silcox, 1968) that single crystal films of these rare-earth metals are usually obtained in a basal orientation (referred to hexagonal axes). Fig. 2 shows a diffraction pattern obtained from a basal (00.1) oriented grain. If we index the pattern with the observed d values and take the structure proposed by Ellinger & Zachariassen (referred to the hexagonal cell the rhombohedral structure has $a=3.63$ and $c=26.2$ Å), we find the indices of the observed diffraction spots to be as indicated in Fig. 2. This shows that the diffraction pattern is not consistent with the rhombohedral structure. Since the rhombohedral structure is referred to a hexagonal lattice, the spots of the type 10.0 (those arranged in the inner hexagonal grid) should not be present because they do not fulfil the criterion for the presence of a reflexion, namely $-h+k+1=3n$ (n being any integer). These forbidden spots can, however, appear as a result of double diffraction. Close examination reveals that if we translate any of the 11.0 type spots (arranged on the outer hexagon) parallel to any diffraction vector so that it coincides with the direct beam, none of these spots occupies a position of an 10.0 type of spot. Thus, we find that there are no primary spots that could produce the 10.0 type of spots by double diffraction (see Andrews, Dyson & Keown, 1968). Hence the above diffraction is not consistent with a rhombohedral structure. If, however, we take an h.c.p. structure, we find that all the spots recorded are consistent with it since there is no extinction condition in this structure for the observed set of reflexions. To verify this further a single-crystal diffraction pattern from a non-basal orientation was taken (Fig. 3); the indexing of this pattern is based on the h.c.p. structure. The diffraction pattern corresponds to an $01\bar{1}1$ reciprocal lattice net. The observed d values and the interplaner angles are in agreement with those expected from an h.c.p. structure; we could not match them on the basis of a rhombohedral structure.

The above diffraction analysis seems to indicate that the thin samarium films have an h.c.p. structure and not the rhombohedral structure which is the only structure known until now. Further evidence for the h.c.p. structure came from studies of dislocation motion and deformation. Their behaviour is similar to that observed in another h.c.p. rare-earth metal, gadolinium (Srivastava & Silcox, 1968; Srivastava & Kumar, 1968). The average calculated values of the a and c parameters, based on the diffraction patterns reported here are: $a=3.65$ and $c=5.86$ Å. These agree with the parameters ($a=3.63$ and $c=5.82$ Å) deduced from the structure model suggested by Ellinger & Zachariassen, and Daane *et al.* In the present investigation the h.c.p. structure was found to persist for all thicknesses of film transparent to 80 to 100 kV electrons. The present observation also suggests that the h.c.p. structure is the only structure found in thin films; there is no clear evidence to suggest a mixture

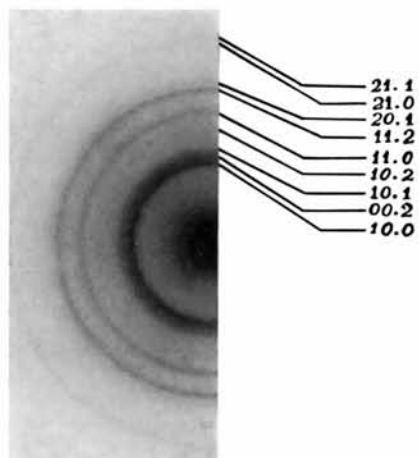


Fig.1. Electron diffraction pattern from a polycrystalline samarium film.

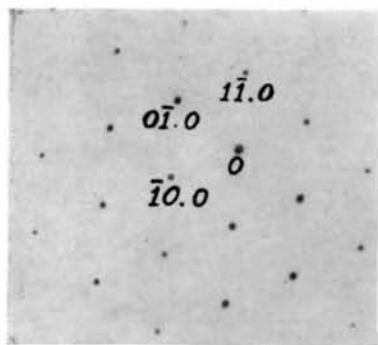


Fig.2. Single crystal diffraction pattern from a basal plane.

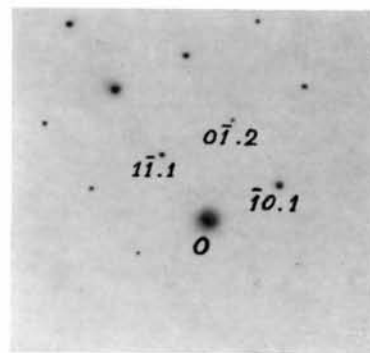


Fig.3. Single crystal diffraction pattern from a non-basal plane.

with any other phase. The observations do not lend support to the submicroscopic twinning description of the structural layers proposed by Daane *et al.* Investigations are currently under way employing X-ray diffraction and electron diffraction techniques, to find out whether the h.c.p. structure is present only in thin films or whether it exists in bulk specimens as well and also to determine the factors which influence the stabilization of this new h.c.p. structure.

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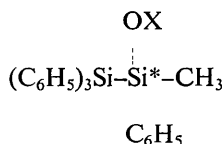
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Crystal data for (—)-1,2,2,2-tetraphenyl-1-methyl-disilanol. By ULRICH DE LA CAMP and HÅKON HOPE, Department of Chemistry, University of California, Davis, California, 95616, U.S.A.

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(—)-1,2,2,2-Tetraphenyl-1-methyl-disilanol, $C_{25}Si_2OH_{24}$, crystallizes in the monoclinic space group $P2_1$ with unit-cell dimensions $a = 20.03$, $b = 11.40$, $c = 20.29$ Å and $\beta = 96.24^\circ$. There are eight molecules in the unit cell.

(—)-1,2,2,2-Tetraphenyl-1-methyl-disilanol (Ia) was prepared by allowing diastereomeric phenylmethyl(—)-menthoxychlorosilane to couple with triphenylsilyllithium, yielding (\pm)-1,2,2,2-tetraphenyl-1-methyl-1-(—)-menthoxydisilane (Ib). The details of the synthesis, the resolution of



I (a) X=H; (b) X=(—)-menthyl, $C_{10}H_{19}$

the mixture of diastereomers, and the conversion to the disilanol have been described by Sommer & Rosborough (1967). Tentative relative configurations were assigned to a series of disilane derivatives; however, serious discrepancies between the chemical and ORD* evidence make these assignments doubtful. No absolute configurations have as yet been given for any of these compounds. Preliminary crystallographic work on (Ia) was therefore started.

* Optical rotatory dispersion.

The space group was determined from oscillation, Weissenberg and precession photographs. Symmetry and systematic absences ($0k0$ absent for $k = 2n + 1$) indicate the space group to be $P2_1$. Cell constants were determined from χ , φ and 2θ values for axis reflections measured on a Picker diffractometer. The radiation used was $\text{Cu } K\alpha$ ($\lambda = 1.542$ Å). The crystals are prisms elongated along **b**.

The crystal data are as follows: $a = 20.03 \pm 0.02$, $b = 11.40 \pm 0.02$, $c = 20.29 \pm 0.02$ Å; $\beta = 96.24 \pm 0.05^\circ$; $V = 4606$ Å³; $Z = 8$; $d_{\text{obs}} = 1.14$, $d_{\text{calc}} = 1.15$ g.cm⁻³.

Owing to the large number of molecules in the unit cell, (leading to 112 non-hydrogen atoms in the asymmetric unit) a detailed structure analysis would appear to be rather costly. We have no immediate plans for further work on this compound.

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