superconductor;  $\rho$  suddenly decreases below 5.5 K and tends to zero below 2 K. Nevertheless, the amount of the decrease of  $\rho$  is found to depend on the surface state. The sample which is gently rubbed by a soft tissue paper so that it becomes more shiny immediately before mounting on the sample holder, has much smaller decrease of  $\rho$ . This is shown for  $\rho$ of  $Ce(In_{0.5}Sn_{0.5})_3$ . Curve A is with this rubbing and curve B is without. Thus we conclude that the superconducting state is not due to bulk sample, but is due to deposits of In-Sn alloy on the sample surface. These deposits are likely to be the eruptions on the sample surface observed by scanning electron microscope. In Ce $(In_{0.3}Sn_{0.7})_3$ , the decrease of  $\rho$  is clearly seen to have two steps. This is understood because the In-Sn alloy is eutectic and  $In_{0.3}Sn_{0.7}$  consists of two components with different compositions and with different superconducting temperatures. The values of these two temperatures are near to those reported [2] on In-Sn alloys, and prove a small amount of this alloys actually deposited on sample surface.

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### D12

## A New Family of Sheet Structures: the Oxyselenides Formed by a Rare Earth and a Second Metal

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Sheet structures are observed in oxyselenides formed by La and a second metal of the IIIA–VA groups of the periodical classification.

{(LaO)GaSe<sub>2</sub>} orthorhombic pseudo tetragonal cells of the (LaO)GaSe<sub>2</sub> (LaO)InSe<sub>2</sub> type

- $(LaO)_4Ge_{1.5}Se_5$ : orthorhombic cell of the  $(NdO)_4-Ga_2S_5$  type, with disordered arrangement of Ge atoms on the Ga sites.
- (LaO)<sub>2</sub>SnSe<sub>3</sub>: orthorhombic pseudo tetragonal cell of the (LaO)<sub>2</sub>SnS<sub>3</sub> type.
- (LaO)SbSe<sub>2</sub>: tetragonal cell of the (CeO)BiS<sub>2</sub> type.

All these structures are formed by alternating (LaO) sheets and  $(M_xSe_y)$  sheets (M = second metal). The (LaO) sheets are formed by La<sub>4</sub>O tetrahedra which

share 4 of their 6 edges in a tetragonal or pseudo tetragonal arrangement. The  $(M_x Se_y)$  sheets are formed by 2, 3 or 4 layers of Se atoms. The M atoms are only bonded to Se atoms, in octahedral (Sb) or tetrahedral (Ga, In, Ge, Sn) arrangements. Similar compounds are not obtained with the other rare earths. The structure of (LaO)GaSe<sub>2</sub>, which is only observed with selenides, is described: the cell is orthorhombic space group P<sub>21</sub>ab; a = 5.951(3); b =5.963(3); c = 12.256(7) Å; Z = 4;  $d_x = 5.84$  Mg m<sup>-3</sup>; M (MoK $\alpha$ ) = 31.3 mm<sup>-1</sup>.

The structure was established on single crystal data and refined by a least-squares procedure; the final R value is 0.07 on 523 independent reflections. The structure is formed by alternating (LaO) and (GaSe<sub>2</sub>) layers, parallel to the (001) plane.

### D13

# Lanthanide Oxides: Effect of $CO_2$ on the $Yb_2O_3$ Hydration

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Recent results in our laboratory [1, 2] have proved that the heaviest terms of the 4f series oxides undergo bulk hydration and carbonation when exposed to the atmospheric air, in contradiction with the previous literature [3]. The main difference between the lighter and the heavier 4f oxides is related to kinetic aspects.

In the case of the hydration of the  $La_2O_3$ , Rosynek [4] has shown a certain inhibition effect exerted by the CO<sub>2</sub>. In the present paper, the interaction of the Yb<sub>2</sub>O<sub>3</sub> with H<sub>2</sub>O, H<sub>2</sub>O/CO<sub>2</sub> mixtures and atmospheric air has been examined through XPS and TPD measurements. The effect of CO<sub>2</sub> on the hydration of ytterbium sesquioxide is discussed in the light of those results.

Ytterbium hydroxycarbonate was precipitated with NH<sub>3</sub> from nitrate solutions.  $Yb_2O_3$  was finally prepared by calcining the precipitate in air at 873 K. The sample here studied was characterized by X-ray diffraction, thermogravimetric (TG) and differential thermal analyses (DTA), IR spectroscopy and pore size distribution. Data about preparation and characterization are reported in [1].

Details concerning the temperature programmed decomposition (TPD) device are given in [5]. All the experiments were carried out in helium flow (30 ml