

# Tin Clusters under the Electron Microscope – The real Structure of $\text{Ir}_4\text{CoSn}_{18}\text{O}_{19}$ and $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$

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High resolution transmission electron microscopy and single crystal X-ray diffraction studies on  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  show very strong one-dimensional stacking disorder effects with an ordered polytype which shows a doubling of the lattice constant  $c$  in comparison to the undoped ternary compound  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ .

## 1. Introduction

Since the discovery of  $\text{M}_3\text{Sn}_{15}\text{O}_{14}$  [ $\text{M} = \text{Ru}$ [1, 2],  $\text{Os}$ [3]] and  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ [4, 5] oxidic cluster compounds containing condensed  $\text{Sn}_6$ - octahedra have been known. The most striking structural features of all these stannates are corner-linked  $\text{Sn}_6$ - octahedra forming triple or fivefold chains, which are filled with the transition metals. Oxygen atoms link these chains. In addition the structures are filled up with one further Sn atom, which does not belong to the assembly of the chains.

In the compounds  $\text{Ir}_4\text{MSn}_{18}\text{O}_{19}$  ( $\text{M} = \text{Fe}, \text{Co}$ ) and  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  condensed  $\text{Sn}_6$ - octahedra could also be found. Both compounds are characterized by corner-linked  $\text{Sn}_6$ - octahedra forming four and fivefold chains, respectively (Fig.1). In both structures the  $\text{Sn}_6$ - octahedra are only filled by Ir atoms. In contrast to  $\text{M}_3\text{Sn}_{15}\text{O}_{14}$ , where a further Sn atom can be found, in  $\text{Ir}_4\text{MSn}_{18}\text{O}_{19}$  this Sn atom is replaced by transition elements, namely by the Fe and Co atoms.  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  can be described as an addition of  $\text{CoO}$  to  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ . The Co atom occupies the same position as the additional Sn-atom which is only 50% filled in  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ . To get a deeper understanding of the real structure of  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  HRTEM investigations have been performed.

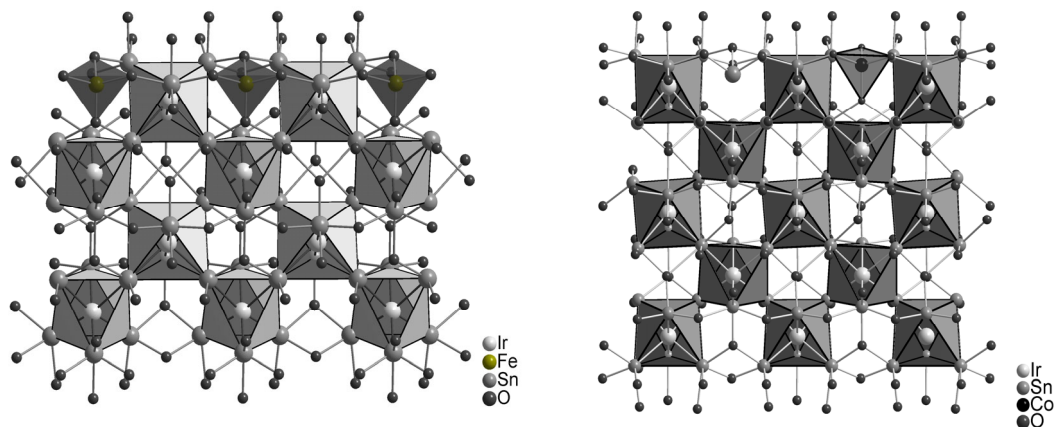


Fig. 1 Left: Crystal structure of in  $\text{Ir}_4\text{CoSn}_{18}\text{O}_{19}$ ,  $[\text{IrSn}_6]$ -chains along  $[100]$ , tetrahedra:  $[\text{MO}_4]$ ; right: idealized crystal structure of  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$ .

## 2. Experimental Details

Single crystals of  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  compound were synthesised in evacuated sealed quartz glass ampules containing an alumina tube with a mixture of  $\text{IrO}_2$ ,  $\text{SnO}_2$  and  $\text{Co}_2\text{O}_3$  in and excess of tin. The resulting tin melt was annealed for one day at 1173 K and cooled down to 973 K over 300 hours. The single crystals could be isolated by dissolving the tin in hot hydrochloric acid. Powder materials of  $\text{Ir}_4\text{CoSn}_{18}\text{O}_{19}$  were prepared by annealing a stoichiometric mixture of  $\text{IrO}_2$ ,  $\text{SnO}_2$  and  $\text{Co}_2\text{O}_3$  and Sn at 1173 K for four days. The resulting materials were checked by powder X-ray diffraction (XRD).

The samples were characterized by high-resolution electron microscopy (HREM) and selected area electron diffraction (SAED). The crystallites were dispersed in *n*-butanol. One drop of the suspension was placed on a perforated carbon/copper net, which was dried carefully, leaving the crystallites in a random orientation. The electron microscopy studies were performed using a Philips CM30/ST instrument (spherical aberration constant  $CS = 1.15$  mm) equipped with a  $\text{LaB}_6$  cathode. At 300 kV, the point resolution is 0.19 nm. SAD patterns were obtained using a diaphragm that limited the diffraction of the selected crystallite to a region of 125 nm in diameter. The kinematical electron diffraction patterns were calculated with the program EMS [6]. EDX-analysis carried out on several single crystals and

powder materials of both compounds on a Philips XL30 ESEM scanning electron microscope (acceleration voltage, 25 kV; SE mode detection) revealed the presence of all expected elements including some traces of Fe. (Fig. 2).

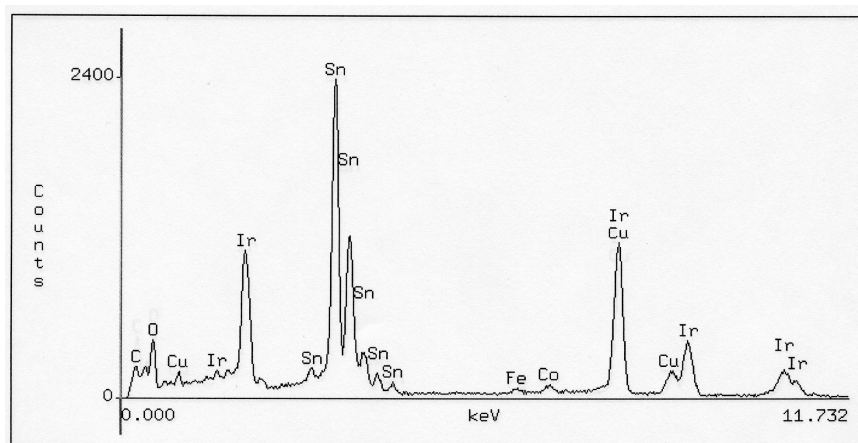


Fig. 2 EDX spectrum of  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$

## 3. Results and Discussions

$\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  shows strong one-dimensional disordered stacking of ordered clusters with an ordered polytype which shows a doubling of the lattice constant *c* in comparison to the undoped ternary compound  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ . As the building blocks of the real structure two different (001) layers A (undistorted cluster layer) and B (distorted cluster layer) could be found (Fig. 3). These A and B layers have the thickness of a cluster layer formed in  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ . The stacking of the layers along  $[001]^*$  is in a random order (Fig. 3 left), but domains with preferred AA- (BB-) and AB sequences can be observed. In bright-field images these lamellas were pictured as broad stripes. As expected the Fourier transform of images of layers containing a random stacking order show very strong diffuse signals along  $[001]^*$ , (Fig. 3 right). The one-dimensional disordering can be confirmed by electron scattering in many directions  $[uv0]$ . By investigating large areas of a crystallite the SAED diagrams show diffuse  $[00l]^*$  streaks similar to the Fourier transforms.

Mixing of A- and B- cluster layers only cause low differences in contrast between simulated and experimental high resolution images. These differences which correspond to very small distortions of the cluster layers are caused by doping of  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$  with Co and Fe. The

doping itself cannot be detected directly with the HRTEM investigations done so far. Detailed simulations need to show if the doping and position of the oxygen atoms in the structure can be imaged under experimental conditions (orientation, crystal thickness, focus etc.).

By increasing the crystallite thickness the significance of the layer variations in simulation and experiment are increased because in thicker sample areas more clusters are superimposed and therewith the distortion appears more significant. Such strongly pronounced thickness depending phenomena are unusual but support the real structure model chosen. In case of two-dimensional real structures such as polysynthetic twinning the difference in contrast is significant in both thick and thin crystal areas.

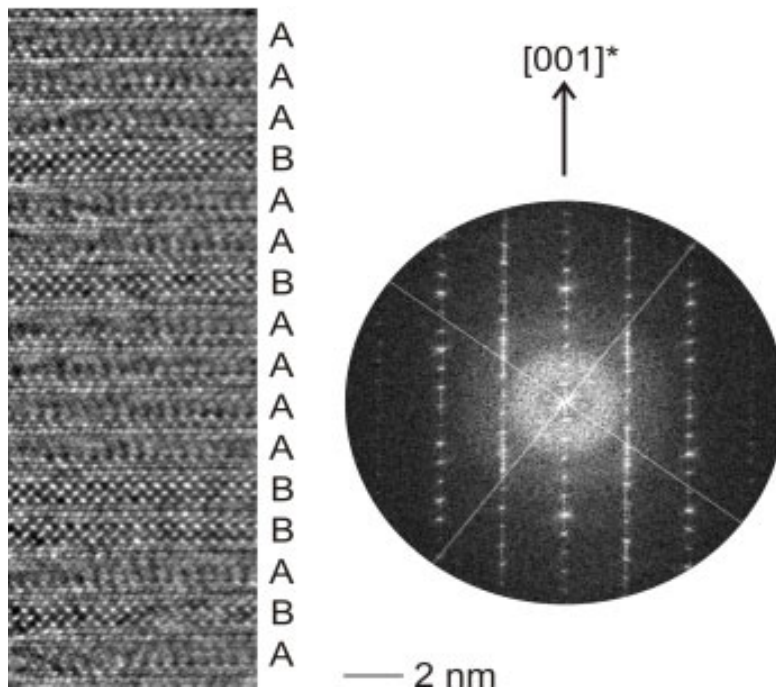


Fig. 3 High resolution micrograph (zone axis  $[010]$ ) of  $\text{Ir}_{10}\text{CoSn}_{45}\text{O}_{45}$  with random stacking of two layers A and B; right: Fourier transform

Some questions remain unsolved and should lead to further investigations. For example it is not clear if a distortion along a cluster layer can vary. It seems reasonable that the distortion of the cluster layers is directly connected to the doping and different amounts of doping may cause different distortions. This would extend the picture of a one-dimensional disordering and would need to consider two new ordering parameters: 1) one ordering parameter *within* the layer, 2) one ordering parameter *between* the layers. Qualitative results about these parameters can be obtained from first

HRTEM investigations already: The ordering parameter within the layer is dominating the real structure. Therewith the model of a one-dimensional disordering with a maximal ordering parameter is certainly a good approximation. Between the layers arrangements with alternating strong and weak distorting are dominating which means there are strong correlations present as well. Investigations with high resolution Z-contrast may be able show if an alternation of strong and weak doped cluster layers are alternating in the structure.

The investigations gave some evidence about a further two-dimensional real structure variation, see Fig. 3. The inter-growth of two different types of layers leads to the formation of lamellas. One of the layers can be identified as the cluster layer formed in undistorted  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$ , the structure of the second layer remains unidentified so far. Simulation calculations show that this cluster layer is neither a distorted version of  $\text{Ir}_{10}\text{Sn}_{45}\text{O}_{44}$  nor a variation of the cluster layer thickness as seen in  $\text{Ir}_4\text{FeSn}_{18}\text{O}_{19}$ . The main difference between the two types of inter-growth can also be seen in Fourier transform. In contrast to first kind of inter-growth diffuse signals can only be observed in every second line perpendicular to  $[001]^*$ . If it would be possible to perform some HRTEM investigations on crystallites showing the second kind of inter-growth the structure could be solved by using high resolution images.

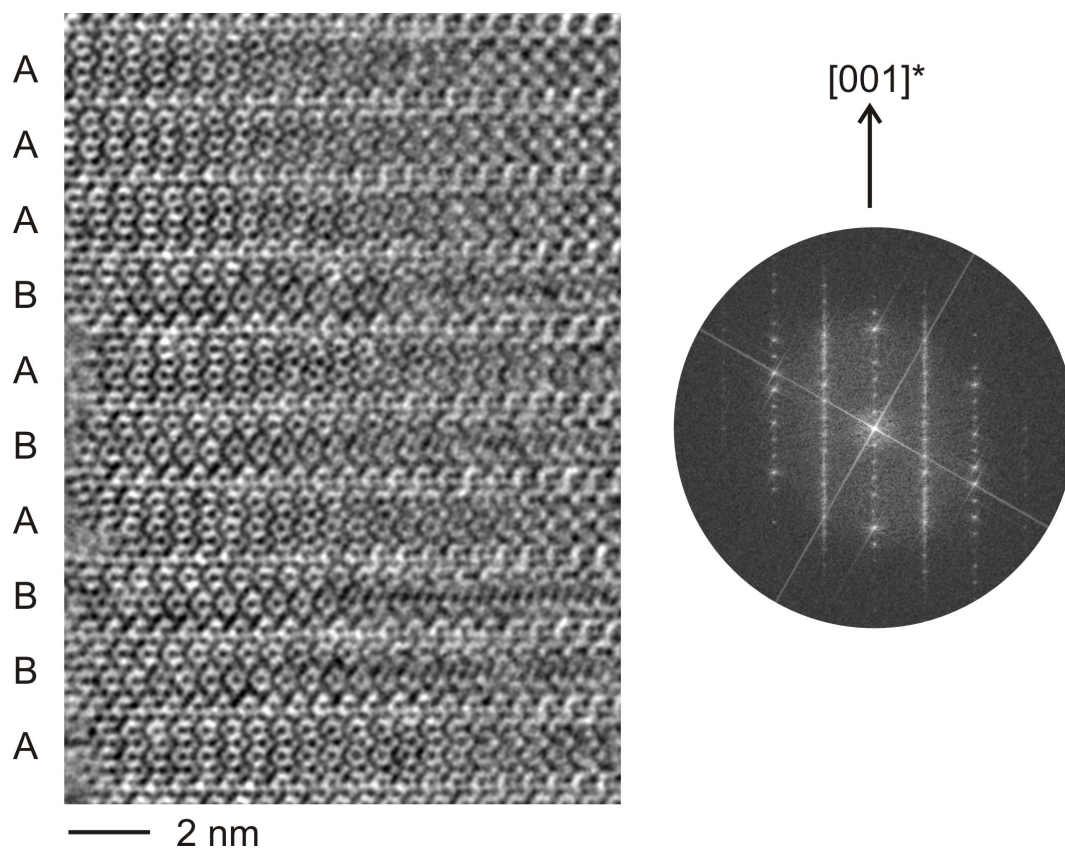


Fig. 4 A alternative two-dimensional real structure. Left: HRTEM for [010] of A layers ( $\Delta f \sim -30$  nm) and B-layers with unknown structure; right: Fourier transform of a bigger quadratic area

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