

09.5-12 LANTHANOID CARBIDE-HALIDES - THE BORDERLINE FOR METAL-METAL BONDING. By Hj.Mattausch, C.Schwarz, A.Simon, Max-Planck Institut für Festkörperforschung, D-7000 Stuttgart-80, FRG

The lanthanoids form various metal-rich halides. With few exceptions, such as  $Gd_2X_3$ ,  $Tb_2X_3$ ;  $X=Cl, Br$ , they are most commonly found as ternary compounds with nonmetals like H, B, C, and N. Especially large is the number of carbide-halides, of which those compounds containing gadolinium were examined in more detail.

The structurally characterized phases are listed in Table 1 according to their "extent of condensation". In this classification scheme lies the fundamental concept that these structures are constructed from edge-sharing  $Gd_6X_{12}$  clusters, in which their centers are occupied by C atoms or  $C_2$  units. Thus, a strong structural correlation with the metal-rich transition metal compounds, e.g.  $ZrCl$ ,  $ZrBr$ , is obtained. When the number of electrons available for metal-metal bonding in clusters of the d-elements is too small, especially for Zr, (e.g.  $Zr_6I_{12}X$  with  $X=B, C$ ;  $Zr_6I_{14}C$ ), one finds nonmetal atoms inserted in these clusters. The number of electrons associated with the interstitial nonmetal atoms increases, while the number of bonding states in the cluster remains constant. The formalism described here is not a usual one for chemical bonds. Extensive charge transfer from metal to nonmetal occurs especially with the electropositive lanthanoid compounds. Therefore, these structures are alternatively described as a defect NaCl variant: in the usual close-packed arrangement of X and  $C^{4-}$  or  $C_2^{4-}$  ions, the  $Gd^{3+}$  ions occupy the octahedral holes around the more highly charged C species. Using the ionic model, the geometrical details of these structures can be simply explained, (e.g. the shifting of the C atoms from the centers of the octahedra, the distortion of the octahedra, etc.). Very importantly, a prediction of the  $C_n$  species is possible from the electron balance with a knowledge of the composition: so in  $(Gd^{3+})_{10}(Cl^-)_{18}(C_2^{6-})_{24}$  there is a C-C single bond, in  $(Gd^{3+})_2(Cl^-)_2(C_2^{4-})_2$ , a C-C double bond. In some compounds up to 3 valence electrons per formula unit remains in metal-centered states, e.g. in  $(Gd^{3+})_3(I)_3C^{4-} \cdot (e^-)_2$ . These can partially occupy bonds with metal-metal bonding character, as is well known for  $Gd_{10}Cl_{18}C_4$ . There now results a simple picture of their chemical bonds: the strong heteropolar Gd-C and Gd-X interactions are supplemented by the relatively weak metal-metal bonds.

Table 1

	Edge sharing Octahedra	$d_{Gd-Gd}$ [pm]	C-Species
$Gd_{10}Cl_{18}C_4$	two	321-409	$C_2^{6-}$
$Gd_{10}Cl_{17}C_4$	two	312-401	$C_2^{6-}$
$Gd_{10}I_{16}C_4$	two	328-400	$C_2^{6-}$
$Gd_{12}X_{17}C_6$ ( $X=Br, I$ )	$\frac{1}{\infty}$ -chain	319-427	$C_2^{6-}$
$Gd_4I_5C$	$\frac{1}{\infty}$ -chain	333-398	$C^{4-}$
$Gd_6X_7C_2$ ( $X=Br, I$ )	$\frac{1}{\infty}$ -double chain	339-395	$C^{4-}$
$Gd_3I_3C$	$\frac{1}{\infty}$ -double chain	331-391	$C^{4-}$
$Gd_2X_2C_2$ ( $X=Cl, Br, I$ )	$\frac{2}{\infty}$ -layers	345-400	$C_2^{4-}$
$Gd_2Br_2C$	$\frac{2}{\infty}$ -layers	343-382	$C^{4-}$
$Gd_2Cl_2C_3$	$\frac{2}{\infty}$ -layers	340-389	$C^{4-}$
$Gd_2IC$	$\frac{2}{\infty}$ -layers	338-380	$C^{4-}$
$Gd_3Cl_3C$	$\frac{3}{\infty}$ -nets	329-368	$C^{4-}$

09.5-13 STRUCTURES WITH OLIGOMERIC CLUSTERS IN THE INDIUMOXOMOLYBDATES:  $In_{11}Mo_{40}O_{62}$ ,  $In_3Mo_{11}O_{17}$ . By Hj.Mattausch, A.Simon, Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart-80, FRG

Infinite chains of  $Mo_6$ -octahedra condensed via opposite edges are present in the structure of  $NaMo_4O_6$  (C.C.Torardi, R.E.McCarley, J.Am.Chem.Soc. 1979, 101, 3963). The  $Mo_4O_6$  chain can be interrupted by structural disorder in the crystal.

$In_{11}Mo_{40}O_{62}$  is the first compound (Hj.Mattausch, A.Simon, E.M.Peters, Inorg. Chem. 1986, 25, 3428), where discrete cluster anions with four and five condensed  $Mo_6$ -octahedra are arranged in layers, which are stacked in an alternating sequence (fig. 1a). A single oligomeric cluster of five condensed octahedra is shown in figure 1b. All free edges are bridged by O-atoms. The channels between the cluster anions are occupied by linear M-M-bonded polycations  $In_5^{7+}$  and  $In_6^{8+}$ . The layers seen in fig. 1a have the general composition  $In_{n+1}Mo_{4n+2}O_{6n+4}$ , where n indicates the number of  $Mo_6$  octahedra in the oligomeric cluster. The number of Mo-Mo-bonding states can be estimated by suitable fragmentation of the oligomeric cluster into  $Mo_6O_{12} + (n-1)Mo_4O_6$  units (A.Simon in A.K.Cheetham and P.Day (Eds.) Inorganic Solids, Oxford University Press, in print). Accordingly, one expects, besides "homogeneous structures" (i.e. structures with a single type of layers), also structures with clusters of other length. A first confirmation of their existence was provided by high resolution transmission electron microscopy (A.Simon, W.Mertin, Hj.Mattausch, R.Gruehn, Angew. Chem. 1986, 98, 831). An electron microscopic photograph of an  $In_{11}Mo_{40}O_{62}$  crystal fragment shows the alternating sequence of the  $(Mo_6)_4$  and  $(Mo_6)_5$ -layers. Such alternating layer segments occur in ordered regions of  $10^5$  pm extension. In the same sample regions are found in which stacking disorder is recognizable: two consecutive  $In_2Mo_{18}O_{28}$  layers are followed by two immediately adjacent  $In_6Mo_{22}O_{34}$  layers. Another part of the same sample is exclusively made up of identical  $In_6Mo_{22}O_{34}$  layers over distances of  $10^5$  pm. In the meantime, the respective new compound  $In_3Mo_{11}O_{17}$  has been isolated as a homogeneous phase and have been characterized by X-ray crystallography ( $a=3160.8$ ,  $b=948.9$ ,  $c=983.9$  pm).

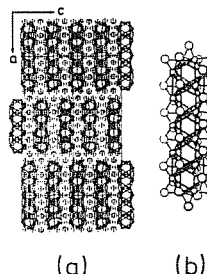


Fig. a: Projection of the crystal structure of  $In_{11}Mo_{40}O_{62}$  on [010]. The oligomeric clusters  $(Mo_6)_4$  and  $(Mo_6)_5$  are arranged in layers (small circles Mo-atoms; large circles with crosses O-atoms). b: Oligomeric cluster with five edgelinked  $Mo_6$  octahedra in  $In_{11}Mo_{40}O_{62}$ .