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The $D1_3$ structure type in intermetallic compounds.

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As part of a study of the MX_4 intermetallic compounds the crystal structures of the following have been investigated: $NaGa_4$, $NaIn_4$, $NaSn_4$, KGa_4, KIn_4, KTl_4, KSn_4, $RbIn_4$ and $CsIn_4$. Results were only obtained for the compounds $NaGa_4$, KGa_4, KIn_4 and $RbIn_4$. A survey is presented of the available data on other MX_4 phases formed by elements of groups I–IIIA with groups II–IVB. It is concluded that the formation of MX_4 phases depends on the position of the element X in the periodic system rather than the atomic size factor or the valency of M.

Continuing the investigation on the crystal structure of the MX_4 intermetallic compounds (Bruzzone, 1965), the behaviour of the alkali metals Na, K, Rb, Cs was examined. Samples of the following compositions were prepared: $NaGa_4$, $NaIn_4$, $NaSn_4$, KGa_4, KIn_4, KTl_4, KSn_4, $RbIn_4$, $CsIn_4$.

The metals used were Na, K, Rb, Cs: 99·9%; Ga, In, Tl, Sn: 99·99%, pure. The alloys were obtained by direct synthesis from stoichiometric quantities of the two metals, melted in sealed Pyrex tubes under a low-pressure atmosphere of very pure argon. The samples were heated to complete fusion and the cooling pattern was dictated by the characteristics of the corresponding phase diagram; for those cases in which the diagram was unknown, the samples were very slowly cooled to room temperature.

All the alloys being very oxidizable, it was necessary to handle them in an inert-gas atmosphere: the specimens for metallographic examination were kept under anhydrous paraffin oil and those for X-ray analysis were sealed in glass capillaries under vacuum. Only $NaIn_4$, KTl_4 and $CsIn_4$ among the prepared alloys appeared to be heterogeneous. The X-ray analysis was not successful in the cases of $NaSn_4$ and KSn_4, which gave very complex powder patterns. However, it was possible to separate needle-shaped single crystals of KGa_4 and to demonstrate the orthorhombic symmetry of this phase. The following lattice constants were obtained by rotation and Weissenberg photographs: $a_0 = 13·86$, $b_0 = 16·02$, $c_0 = 6·49$ Å.

The tetragonal $D1_3(BaAl_4)$ structure-type was found for the phases: $NaGa_4$, KIn_4 and $RbIn_4$. From powder photographs the lattice constants were calculated by the least-squares method and these are listed in Table 1 together with the z parameters obtained by comparison of the calculated and observed intensities of the reflexions.

Table 1. *Lattice constants and z parameters*

Compound	a_0	c_0	c_0/a_0	z
$NaGa_4$	4·223 Å	11·19 Å	2·65	0·381
KIn_4	4·835	12·71	2·63	0·379
$RbIn_4$	4·914	12·82	2·61	0·378

A survey of the available data on the MX_4 phases, formed by an element of the groups IA, IIA, IIIA (rare earth and thorium metals) as component M, with a IIB, IIIB, IVB group element of the periodic system as component X, yields the following information.

(*a*) MX_4 *compounds with* X = II*B group element*

The alkali, alkaline earth and rare earth metals do not form 1:4 phases with zinc and cadmium. Thorium gives a tetragonal $D1_3$-type compound, $ThZn_4$. There are few data on the alloys of mercury, and it is therefore not possible to speculate about the behaviour of the different metals with this element.

(*b*) MX_4 *compounds with* X = III*B group element*

The alkali and alkaline earth metals form the following compounds having the tetragonal $D1_3$ structure type: $NaGa_4$, KIn_4, $RbIn_4$, $CaAl_4$, $SrAl_4$, $BaAl_4$, $CaGa_4$, $SrGa_4$, $BaGa_4$, $BaIn_4$. Among the rare earths only europium and ytterbium (in the divalent state) form 1:4 phases with the above $D1_3$ structure, alloying with aluminum and gallium. The most aluminum-rich compounds, formed by lanthanum, cerium, praseodiumium, neodimium, so far reported as MX_4 ($D1_3$-type), seem to be orthorhombic M_3X_{11} phases (Gomes de Mosquita & Buschow,1967). No MX_4 compounds of thorium with these elements has been identified.

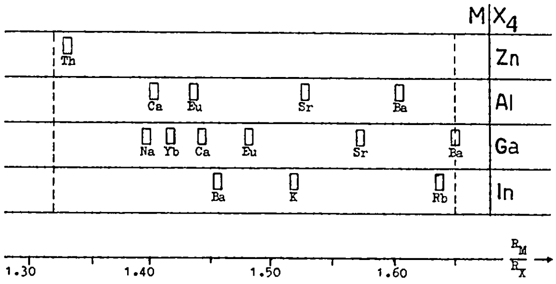
(*c*) MX_4 *compounds with* X = IVB *group element*

Only the alkali metals form some 1:4 phases ($NaSn_4$, KGe_4, KSn_4, $RbGe_4$, $CsGe_4$) (Schaffer & Klemm, 1961) In no case does the $D1_3$ structure type occur.

In conclusion, fourteen MX_4 compounds show the $D1_3$ structure type; thirteen are formed by an X = IIIB group element (Al, Ga, In) and only one by an X = IIB group element (Zn).

As previously described (Bruzzone, 1965), in this structure type the M atoms occupy holes formed by clusters of the X atoms and the favourable atomic size ratio can be calculated from geometrical considerations to be $1{\cdot}32 \leq R_M/R_X \leq 1{\cdot}65$, if the atoms are regarded as rigid spheres in contact. Moreover, the R_M/R_X values, computed for every known phase with the atomic radii of Goldschmidt (Laves, 1956) (using coordination numbers 12 and 8 respectively for the M and X atoms, as the geometry of the unit cell suggests) always fall between 1·34(Th/Zn) and 1·65(Ba/Ga), as Table 2 shows. Therefore, it may be said that the occurrence of this structure is largely controlled by the size factor, which, however, is not in itself sufficient In fact, some 1:4 compositions belonging to the favourable range of atomic size ratio do not correspond to homogeneous phases with this crystal structure. Furthermore, although the existence of the tetragonal ($D1_3$-type) $ThZn_4$ compound could suggest the occurrence of isomorphous (rare-earth) Zn_4 phases, in reality this is not so: only (rare-earth)$_3Zn_{11}$, isomorphous with La_3Al_{11} (Bruzzone, Fornasini & Merlo, 1969), are known (Lott & Chiotti,1966).

Table 2. MX_4 *intermetallic compounds with the* $D1_3$ *structure type*



It is noteworthy that the existence of the $D1_3$ structure type does not depend upon the valency of the M component; but it appears to be related to the position of the X-component element in the periodic system, since of the 14 compounds 13 contain a IIIB group element. From the existence of the $ThZn_4$ phase one could infer that the IIB group elements are able to achieve an electron/atom ratio with metals of the IVA group favourable to the formation of this structure; since the size factor must also be taken into account, the actual possibilities are so restricted that $ThZn_4$ may well be the only case of a $D1_3$ structure in compounds of the IVA group metals.

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