making it difficult to locate the lighter atoms with any precision.

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The Crystal Structures of Mo_2As_3 and W_2As_3

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In the course of the continued studies of the transition metal chalcogenides and pnictides at this Institute an investigation of molybdenum and tungsten arsenides and antimonides has been carried out. The present communication gives a brief description of the crystal structures of the previously unknown phases Mo_2As_3 and W_2As_3. (The phases Mo_4As_5 and W_4As_5 reported by Boller and Nowotny [1] are undoubtedly identical with the phases Mo_2As_3 and W_2As_3, respectively. However, these authors did neither succeed in assigning the correct compositions nor the true crystallographic unit cells to their samples.) The results of the phase analytical studies of these systems and the structural and magnetic properties of the phases Mo_5As_4, $MoAs_2$, Mo_3Sb_7, and WAs_2 are discussed elsewhere.[2-4]

No extended ranges of homogeneity of these phases exist, and the compositions were unequivocally determined to be Mo_2As_3 and W_2As_3. The unit cells are monoclinic with the following dimensions (on the basis of Guinier photograph data taken with strictly monochromatized Cu$K\alpha_1$-radiation):

Mo_2As_3:
$a = 16.061 \pm 0.002$ Å,
$b = 3.2349 \pm 0.0004$ Å,
$c = 9.643 \pm 0.001$ Å,
$\beta = 136.74 \pm 0.02°$

W_2As_3:
$a = 15.966 \pm 0.001$ Å,
$b = 3.2791 \pm 0.0004$ Å,
$c = 9.599 \pm 0.001$ Å,
$\beta = 136.648 \pm 0.006°$

On the basis of the observed densities, 8.07 g cm^{-3} (Mo_2As_3) and 11.32 g cm^{-3} (W_2As_3), the unit cells contain 4 T_2As_3-groups ($Z_c = 4.00$ for Mo_2As_3 and $Z_c = 3.97$ for W_2As_3).

Needle-shaped single crystals (with the diad axis along the needle axis) of Mo_2As_3 and W_2As_3 were obtained by means of transport reactions using traces of bromine as a transport agent. The crystal structures were solved on the basis of integrated Weissenberg photographs of the *h*0*l* and *hll* reflections using direct methods for sign determination. (Attempts to derive trial structures from examination of Patterson syntheses and difference Patterson synthesis were unsuccessful.) The atomic arrangement in the crystal structures of Mo_2As_3 and W_2As_3 in terms of the space groups $C2/m$ is as follows (all atoms in position $4(i)$):

Mo_2As_3:
Mo_I with $x = 0.248$, $z = 0.125$
Mo_{II} with $x = 0.351$, $z = 0.567$
As_I with $x = 0.127$, $z = 0.207$
As_{II} with $x = 0.415$, $z = 0.144$
As_{III} with $x = 0.104$, $z = 0.580$

W_2As_3:
W_I with $x = 0.248$, $z = 0.124$
W_{II} with $x = 0.348$, $z = 0.567$
As_I with $x = 0.125$, $z = 0.204$
As_{II} with $x = 0.417$, $z = 0.147$
As_{III} with $x = 0.105$, $z = 0.579$

Details of the structures and discussion of the chemical bonding will be published in a forthcoming paper.

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