

Fig. 10. Schematic presentation of the domain regions of structures *A*, \bar{A} and *B* respectively in the investigated crystal grain.

tallography (1952), for space group *Pmnb* the relationship $p=\frac{1}{4}$, $q=\frac{1}{4}$, $r=\frac{1}{4}$ exists. Therefore, the transformation of the coordinates of the setting of this paper (designated as x, y, z) into that of the usual setting (designated as x', y', z') is given by

$$\begin{aligned}x' &= x + \frac{1}{4} \\ y' &= y + \frac{1}{8} \\ z' &= z.\end{aligned}$$

Pmnb can be transformed into the standard notation *Pnma* by $a \rightarrow b$, $b \rightarrow a$, $c \rightarrow -c$.

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Polycrystals and Stereochemistry of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ *

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Based on the results of the preceding paper by H. Schulz & F. A. Schröder [*Acta Cryst.* (1973), **A29**, 322–333] the diffuse diffraction pattern of crystals of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ as observed by L. O. Atovmian & Z. G. Aliev [*Zh. Strukt. Khim.* (1971), **12**, 732–734] is explained. Furthermore the types of polycrystals which can be expected to exist are deduced. This leads to a detailed understanding of the stereochemistry of this compound. Several aspects of the crystal growth are discussed.

Introduction

A characteristic of the stereochemistry of molybdenum and tungsten is structures built of endless chains of octahedra by sharing two *trans* vertices. Only compounds of these two elements in the oxidation state + VI form such structures using only monatomic ligands such as oxygen and halogen atoms at the vertices of electrostatically neutral octahedra.

According to the most recent results for the determination of the structure of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ by Atovmian & Aliev (1971), Schröder & Nørlund Christensen (1972) and Schulz & Schröder (1973) this compound also forms such chains of octahedra. These have mixed ligands and the composition $\text{MoCl}_2\text{OO}^{2/2}\text{OH}_2$. In the following some stereochemical aspects of these chains are discussed.

Results

In the preceding paper of Schulz & Schröder (1973) the results of a structural investigation of a polycrystal

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of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ are described. It has been proved that crystal grains of this compound may contain regions of three different structures, called *A*, \bar{A} and *B* (cf. Figs. 2, 8 and 9 respectively, of the preceding paper).

The crystals investigated by Schröder & Nørlund Christensen (1972) and Schulz & Schröder (1973), which showed the structures *A*, \bar{A} and *B*, were grown from the vapour phase by passing a slow stream of HCl gas over MoO_3 at about 600°C. Atovmyan & Aliev (1971) who determined structure *A*, obtained the investigated crystals (together with those of MoO_2Cl_2) during the zone melting of MoO_2Cl_2 powder. They found, that 'with the exception of one crystal, reflexions of the type $h+k+l=2n+1$ had the form of diffuse spots on the X-ray diffraction patterns of a large number of selected crystals'. This observation will be explained in the following by consideration of the structural features of the compound $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ as determined by Schulz & Schröder (1973).

The structures *A*, \bar{A} and *B* are built up by chains of the same irregular octahedron: an off-centre Mo atom with two chlorine atoms, one oxygen atom and one water molecule as terminal ligands and two bridging oxygen atoms. The differences between these three structures are the result of two factors: (1) The alternating way in which the off-centre Mo atom (and its closest coordination ligands) is placed with respect to the geometric centre of the octahedron. This produces structures *A* and \bar{A} : (2) The enlargement by a factor of four of the unit-cell dimension along the chain direction. This enables the realization of 'mixtures' of the arrangements of structures *A* and \bar{A} within the larger unit cell, thus producing structure *B*.

Discussion

The occurrence of the diffuse reflexions obtained by Atovmyan & Aliev (1971) points to the existence of antiphase domains in structure *A*, which means that the origin of structure *A* is shifted by a vector $\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c}$, if the atomic arrangements of structure *A* within two antiphase domains are compared. For this comparison it is necessary to study the antiphase domains with respect to a common origin. If each atom (cf. Table 4 in the preceding paper) is shifted by $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, the structure shown in Fig. 1, which is drawn in a slightly schematic way, is obtained. The comparison of this Figure with Fig. 2 of the preceding paper shows that the positions of all atoms with the exception of those of the Mo atoms are not altered. Only the Mo atoms are shifted in the direction of $+\mathbf{b}$ or $-\mathbf{b}$ in such a way that the relative orientation of their closest bonding polyhedra (which are the tetrahedra) has been changed. Thus, the antiphase domains have to be understood as being caused almost solely by the Mo atoms. The coordination octahedra around the Mo atoms do not change their shapes significantly during the transition to an antiphase domain.

The extension of this result to the structures \bar{A} and *B* seems to be allowed. This means that the existence of antiphase domains in these two structures has to be

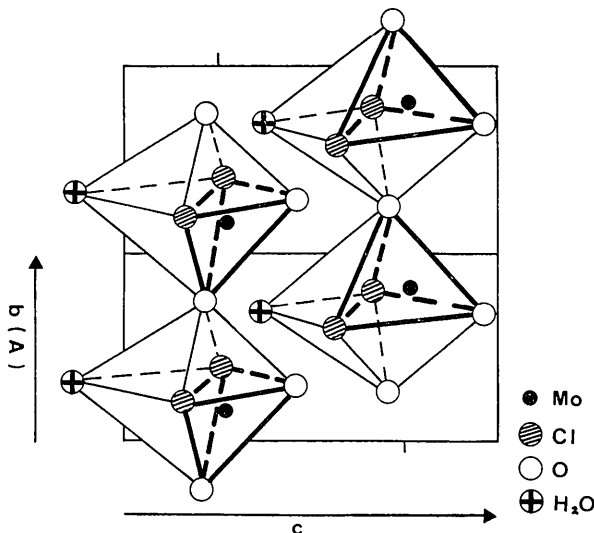


Fig. 1. Antiphase domain structure of structure *A* (schematic). Two unit cells are drawn.

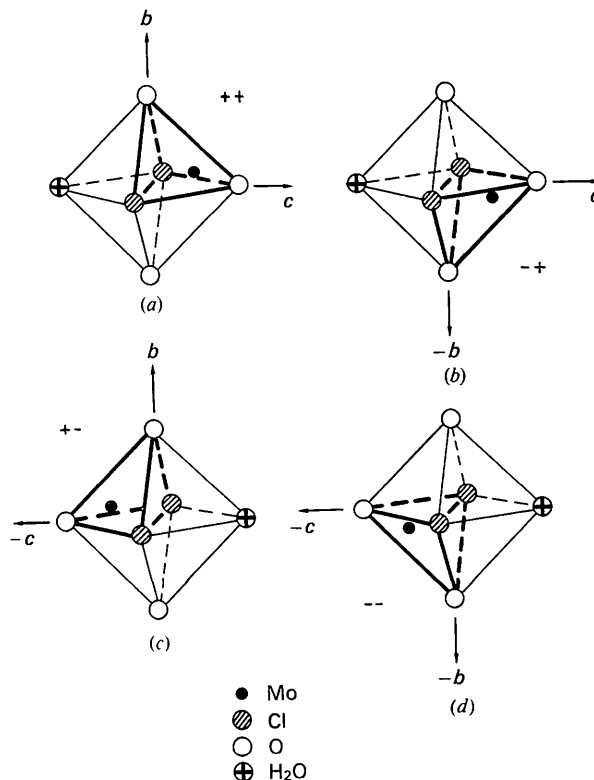


Fig. 2. Schematic presentation of the possibilities of positional distribution of Mo and its ligands in an isolated coordination octahedron. Each of these occurs as a member of chains of octahedra. The common (bridging) O atoms are always drawn at top and bottom.

assumed as well. The reason why in the crystals investigated as described in the preceding paper no anti-phase domains have been detected so far may be because each single domain covers too large a crystal volume. Improved experiments to check their existence are in progress.

The experimental results obtained so far allow a more systematic treatment of the stereochemical characterization of the coordination octahedron under discussion:

(1) As shown by the bond lengths the octahedron includes in each case a coordination tetrahedron (also irregular) around the Mo atom. The ligands are always both Cl atoms, the terminal O atom and one (the closer) bridging O atom.

(2) This tetrahedron is not orientated at random. As the experimental results show, the Mo atom and the specified O atoms always lie on a mirror plane. Each Mo atom has four possible sites upon it: the Cl

and O atoms follow each special arrangement so as to conserve the rigidity of this tetrahedron. It is believed that the water molecule does not contribute very much to this rigidity.

This behaviour can be put into a simple formalism in the following way. In Fig. 2(a), one octahedron of structure *A* is drawn in a very schematic way. If a two-dimensional Cartesian coordinate system is placed therein as also indicated in Fig. 2(a), then the tetrahedron outlined therein may be denoted by ++. The possible other arrangements are given in Fig. 2(b), (c) and (d) respectively and are denoted as shown there. This allows a description of the orientation of the particular tetrahedron relative to the sequence of the two (antiparallel) chains of octahedra which exist in all structures in the manner given in Fig. 3.

These results lead to one clear conclusion: to each orientation of the coordination polyhedron within one chain, there corresponds the same or almost the same site energy, while the site energy for the two chains within the unit cells is lowest for an antiparallel arrangement. How can this be understood? Firstly, it is possible that structure *B* is generated from one of structures *A* and \bar{A} by a site change between a water molecule and an oxygen atom. In structures *A* and \bar{A} the water molecules lie on rods parallel to the *b* axis. The same is true for the terminal oxygen atoms. In structure *B* the corresponding rods (*cf.* Figs. 2, 8 and 9 respectively of the preceding paper) have mixed occupancy of water molecules and oxygen atoms.

It might be supposed that the crystal growing starts with a unit cell of structure *A*. During this process in a polyhedron, a water molecule and the terminal oxygen atoms can change positions by surface diffusion. It might be assumed that this site change takes place for example after the growth of one cell of structure *A* (subcell 1 as labelled in the preceding paper) and during the growth of subcell 2 at the right polyhedron (*cf.* Fig. 9 (from the bottom) in the preceding paper). As a consequence of this site change, the Mo atom will move from the right side of the octahedron to the left side. This now corresponds to the arrangement of the tetrahedra of the right chain of structure \bar{A} as shown in Fig. 8 of the preceding paper. If the crystal growth is assumed to be in this way, it produces the arrangement as in the first and second subcells of structure *B*. These two subcells may serve as nucleus for structure *B*. The growth of structure *B* can be interrupted by the growth of structure *A* for a greater number of unit cells. In this case, subcell 1 plays the role of a nucleus. Structure \bar{A} is generated if subcell 3 acts as nucleus. In this way, a crystal grain may contain parts of structures *A*, \bar{A} and *B*. These structures are orientated with respect to each other in such a way that the main reflexions are superimposed. Furthermore, the reflexion intensities of structures *A* and \bar{A} are equal. It was concluded that such crystal grains were the objects of investigation by Schröder & Nørnlund Christensen (1972) and Schulz & Schröder (1973).

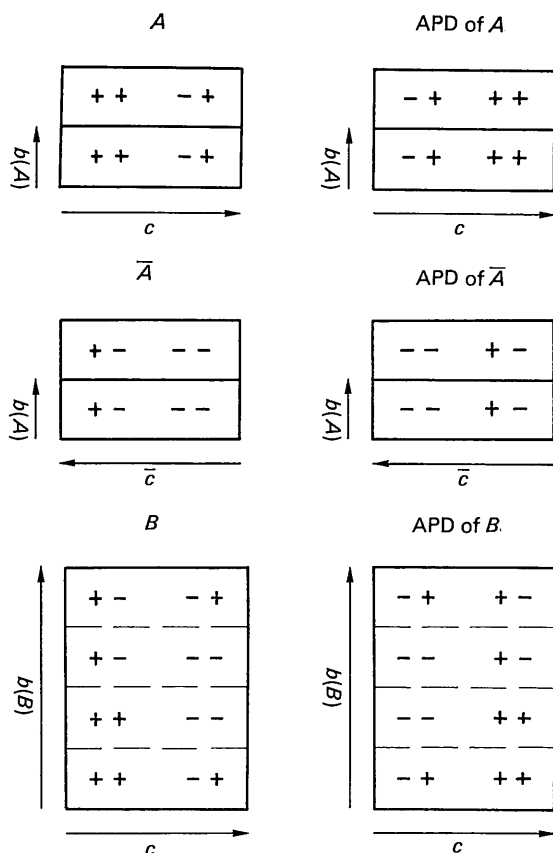


Fig. 3. Systematic presentation of the positional orientation of the coordination polyhedra of the different structures of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$. (This schematic drawing should be considered in comparison with Figs. 2, 8 and 9, respectively, of the preceding paper.) The chains of octahedra run from bottom to top. Solid horizontal lines give the extension of the unit cells. Alternative possibilities for variations of structure *B* according to Table 2 of the preceding paper, are not drawn.

Unfortunately, however, nothing is known about the species existing in the vapour phase from which the crystals investigated in these two papers were grown. So it may be possible that the growth species has the formula unit $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$. This is supported by the further result that the compound can be sublimed in a tube moved back and forth in a stream of HCl gas (Schröder, 1969). Thus it evaporates congruently and when the crystals of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ grow again, the 'components', MoO_2Cl_2 and H_2O , should be almost exactly in a 1:1 ratio, and thus the formula unit $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ can at least be regarded as the quasi growing species.

The method of preparation of Schröder & Nør-lund Christensen (1972) supplies most of the crystalline material as a semicrystalline product (Schröder, 1969). This can be understood if it is assumed that every product of crystallization of $\text{MoO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ is a result of the possibilities of orientation in which this formula unit can be placed. These possibilities could be described as a rotational degree of freedom with adjustment in two positions of the described polyhedra of structures *A* and \bar{A} .

It was found by Schröder & Nør-lund Christensen (1972), that at 155°C structure *B* is irreversibly transformed into structure *A* (and \bar{A}). This may take place by a mere rotation of some polyhedra within the unit cell of structure *B*. As a consequence, it has to be concluded that the two positions of the water molecule are also equal in their site energy and only the 'longer-range order' between two polyhedra within the chains corresponds to a somewhat higher energy in structure *B* than in structures *A* and \bar{A} .

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The Effect of Fast-Neutron Irradiation on Zr_4Al_3

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The effect of fast-neutron radiation on the structure of Zr_4Al_3 has been studied using X-ray diffractometry. The changes in line intensity are explained by the disordering caused by the replacement of 0.5 atom in zirconium sites by aluminum. The anisotropic changes in the size of the unit cell can be partially explained by the geometrical changes produced by the disordering of atoms of unequal size.

Introduction

The effect of fast-neutron irradiation on the structure of the intermetallic alloy having the composition Zr_4Al_3 has been investigated using X-ray powder diffraction methods. The aim of the study was to compare the effects of fast-neutron irradiation in this alloy with those produced in the binary σ phases already investigated by similar techniques (Wilson & Parselle, 1965; Spooner, 1968). A characteristic feature of the structure of the σ -phase alloy and Zr_4Al_3 is the vertical row of transition-metal atoms whose separation is much less than that normally encountered in intermetallic structures. It was hoped that a comparison of the damage in both structures would lead to a better un-

derstanding of the importance of these atoms in their respective structures.

Experimental

Samples of Zr_4Al_3 powder were irradiated in aluminum capsules in the HIFAR reactor at A.E.E.C., Lucas Heights, New South Wales, to nominal doses of 10^{19} and 10^{20} fast neutrons (>1 MeV) at the operating temperature of the reactor ($\sim 60^\circ\text{C}$). The Debye-Scherrer powder films taken of the specimens before and after irradiation were used mainly for reference purposes. Measurements of lattice parameters and line intensities were made on diffractometer traces, all taken at the same speed and with a fairly long time constant. Reproducibility was good and average values of 2θ readings were taken from three charts run under similar conditions. Lattice parameters for the irradiated

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