CRYSTAL STRUCTURE OF CADMIUM TUNGSTATE CdWO$_{4}$

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Abstract

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CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF CADMIUM TUNGSTATE $CdWO_4$

The single crystals of Cd tungstate placed at our disposal were synthesized under hydrothermal conditions from the system $CdO–WO_3–LiCl–H_2O$ at temperatures of 300-500°, pressures of 1000-1500 atm, and LiCl concentrations up to 16 wt.% ([1]).

Cadmium tungstate is an "extreme" representative in the subgroup of monoclinic tungstates with "medium" divalent cations (Mg, Co, Ni, Fe, Zn, Mn, Cd), which, with the formula ABX_4, crystallize in the structural type not of scheelite, but of wolframite* (Fig. 1 ([2])).

In a monoclinic cell with parameters $a = 5.02,\ b = 5.85,\ c = 5.07$ Å, $\beta = 91°30'$, there are two formula units of $CdWO_4$.

The fixed X-ray group $2/m\,P—/c$ includes two Fedorov groups: the acentric Pc and the holohedral P^2/c ([3], [4]).

The required set of reflections was obtained with Mo K_α radiation ($\max \sin\vartheta/\lambda = 0.75$ Å^{-1}) from precession photographs of zero layer lines along all three axes (zones $h0l$–80, $hk0$–120, $0kl$–78 nonzero reflections). The intensities were estimated by the usual method of comparison with a blackening scale, taking into account the resolution of K_{α_1} and K_{α_2} according to ([5], [6]). From the Patterson projections $p(xz)$ and $p(xy)$ there followed a centrosymmetric arrangement of the cadmium and tungsten atoms.

Fig. 1. Structural type of wolframite. Chains of octahedra in the ideal structure of α-PbO_2 and $NiWO_4$

Table 1

Coordinates of the basis atoms of Cd tungstate

Atoms	x/a	y/b	z/c
Cd	0.500	0.692	0.000
W	0.000	0.180	0.000

Atoms	x/a	y/b	z/c
O_1	0.210	0.900	0.460
O_2	0.240	0.380	0.380

In the presence of these heavy atoms ($r = \sqrt{\sum f_n^2 : \sum f_l^2} = 5.5$), the phases (signs) of the structure amplitudes ([7], [8]) will be determined by specifying only the "centrosymmetric coordinates" of the heavy atoms, which makes it possible to carry out the calculation of electron-density syntheses within the framework of the holohedral group D^2/c.

The O atoms were localized from difference Fourier series with initial ($F_e - F_{Cd+W}$). The attained discrepancy coefficients for the coordinates of the atoms indicated in Table 1 were $R_{h0l} = 11.7\%$, $R_{0kl} = 11\%$, respectively. The introduction of the usually accepted correction for thermal motion proved possible –

* As an illustration of morphotropic regularities, it may be noted that the Cd molybdate $CdMoO_4$, analogous in formula, as shown by parallel analyses of the authors, crystallizes already in the scheelite type, i.e., with a well-pronounced coordination number 8 for Cd in a tetragonal lattice.

only in the $h0l$ zone for Cd and O atoms ($B = 0.3$ Å^2). For W atoms in the $h0l$ zone and for all atoms in the yz projection, allowance for the thermal factor did not lead to a decrease in R.

For divalent Cd one obtains the usual octahedron, with distances close to those already known (Table 2): 2.18–2.34 Å. For the heavy W atom the coordination polyhedron is very distorted: with 4 O atoms at

Table 2

Interatomic distances in the structure of $CdWO_4$

Cd polyhedron	Distances, Å	W polyhedron	Distances, Å	Cd polyhedron	Distances, Å	W polyhedron	Distances, Å
Cd–$O_5(2)$	2.33	W–$O_6(2)$	1.80	O_2–O_6	3.06	O_1–O_6^1	2.70
Cd–$O_6(2)$	2.34	W–$O_1(2)$	1.87	O_3–O_5	3.30	O_1–O_7	2.90
Cd–$O_2(2)$	2.18	W–$O_2^1(2)$	2.22	O_5–O_6	2.90	O_2^1–O_3^1	3.00
O_2–O_3	3.60	O_1–O_2^1	2.80	O_5–O_7	3.20	O_3^1–O_7	2.83

Fig. 2 and Fig. 3

Figure 1: Fig. 2 and Fig. 3

Cd polyhedron	Distances, Å	W polyhedron	Distances, Å	Cd polyhedron	Distances, Å	W polyhedron	Distances, Å
O_2–O_5	3.36	O_1–O_3^1	2.45	O_6–O_7	2.92	O_6^1–O_7	2.75

distances of 1.80–1.87 Å, two O atoms are displaced to 2.22 Å. An analogous octahedron was found in the structure of $NiWO_4$ ([4]). In earlier works ([9,10]) the two displaced O atoms were usually excluded from the first coordination sphere of W and included in the coordination sphere of Cd, despite the fact that the Cd–O distances for these anions are appreciably larger (up to 3.01 Å) than the sum of the ionic radii $r_{Cd} + r_O = 2.30$–2.35 Å. The O–O distances in the Cd octahedron

Fig. 2. Chain of W octahedra in the structure of $CdWO_4$

Fig. 3. Structure of $CdWO_4$ in polyhedra, larger around Cd. In the yz projection, chains from three stories are shown: in the lower and upper stories, deformed Cd octahedra; in the middle story, more distorted W octahedra

do not go beyond the usual limits; in the tungsten polyhedron, however, two O–O edges, equal to 2.45 Å, are much shorter than the others (see also ([4])): 2.75–3.00 Å. These edges, being common to two neighboring W octahedra (in a chain) (Fig. 2), are, as it were, clamped between two Cd octahedra, and the bond of the Cd cation with the indicated O atoms, as follows from Table 1, is the shortest of all the bonds of the Cd octahedron (Fig. 2).

The structural motif of tungstates of medium cations (structures of the wolframite type) appears clearly in the (xz) and (xy) projections (Figs. 2 and 3). In the ideal case, for compounds ABX_4 we have a two-layer hexagonal closest packing with the plane of the layers perpendicular to the a axis (structural type α-PbO_2). In alternating layers

only half of the octahedral voids of the closest packing are occupied, and within each layer by homogeneous cations, i.e., if in the first layer these are cations A, then in the second they are only cations B. The occupation of the voids is not statistical but regular: in the first layer there is an alternation of a zigzag strip of octahedra empty and occupied by atoms A, and in the second, empty and occupied by atoms B. Above each occupied zigzag column of the lower layer there is an empty one of the upper layer, and vice versa; that is, both within one layer and from layer to layer, occupied and unoccupied octahedral cells alternate.

Closest to the ideal structural motif ABX_4 is the structure of $NiWO_4$, but even in it there is a displacement of the Ni atom from the center of the octahedron along the twofold axis by 0.13 Å, and of W by 0.3 Å. The filling of the octahedra by the larger Cd cations (r_{Cd} = 0.99 Å, r_{Ni} = 0.74 Å) deforms the oxygen packing still more strongly: in addition to a significant displacement of Cd from the center of the octahedron (0.3 Å), the height of the layer with cations A increases from 2.20 in the $NiWO_4$ structure to 2.60 Å in Cd tungstate.

The shortening of two edges of the W octahedra noted above is another clear illustration of Pauling' s crystal-chemical rule on the substantial shortening of shared edges in polyhedra with strong (multivalent) cations.

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Note: Figure translations are in progress. See original paper for figures.