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Space group and cell dimensions of a specimen of hollandite. By BIBHUTI MUKHERJEE, *Geological Survey of India, Calcutta 13, India*

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Hollandite was first described by Fermor (1909) from the Kajlidongri manganese mine, Central India. Crystals of hollandite were found in quartz veins on a matrix of massive cryptomelane (Mukherjee, 1959). Byström & Byström (1950) studied prismatic crystals of hollandite from Swedish manganese ores, and obtained a period of 2.86 Å from rotation photographs ($Cr K\alpha$) about the prism axis. Their Weissenberg photographs showed tet-

ragonal Laue symmetry C_{4h} with $a \approx 9.9$ Å, but the indexing of powder photographs was possible only with the monoclinic cell,

$$a = 9.91, b = 2.872, c = 9.75 \text{ \AA}; \beta = 90.6^\circ$$

for hollandite I and

$$a = 10.00, b = 2.879, c = 9.72 \text{ \AA}; \beta = 91.1^\circ$$

Table 1. Powder spacing data of hollandite, J 941

I/I_1	d (Å)	$\sin^2 \theta$ (obs.)	hkl	$\sin^2 \theta$ (calc.)	I/I_1	d (Å)	$\sin^2 \theta$ (obs.)	hkl	$\sin^2 \theta$ (calc.)
15	6.96	0.0193	101	0.0191	7	1.72	0.3167	503	0.3164
20	4.94	0.0384	002	0.0383	7	1.705	0.3224	503	0.3224
40	3.52	0.0755	202	0.0749	10	1.695	0.3262	305	0.3264
40	3.50	0.0765	211	0.0755	25	1.67	0.3361	600	0.3359
100	3.145	0.0948	112	0.0755	20	1.65	0.3443	006	0.3447
100	3.12	0.0962	112	0.0763	25	1.63	0.3526	025	0.3524
7	3.00	0.1042	202	0.0764	5	1.607	0.3627	324	0.3525
15	2.88	0.1128	301	0.0942	15	1.563	0.3835	125	0.3626
20	2.765	0.1225	103	0.0949	15	1.563	0.3835	522	0.3825
10	2.50	0.1499	103	0.0961	60	1.555	0.3875	116	0.3834
20	2.467	0.1539	212	0.1047	60	1.547	0.3914	206	0.3844
60	2.415	0.1607	310	0.1123	5	1.523	0.4041	522	0.3865
5	2.36	0.1681	020	0.1129	10	1.508	0.4120	225	0.3877
7	2.33	0.1725	120	0.1223	7	1.495	0.4192	225	0.3916
5	2.295	0.1780	311	0.1224	10	1.495	0.4192	612	0.4049
40	2.225	0.1892	021	0.1225	10	1.46	0.4396	424	0.4123
55	2.21	0.1919	400	0.1493	30	1.44	0.4517	216	0.4127
70	2.18	0.1971	220	0.1502	10	1.425	0.4613	424	0.4186
60	2.165	0.1998	213	0.1530	15	1.415	0.4681	514	0.4187
5	2.115	0.2093	004	0.1533	10	1.415	0.4681	325	0.4392
15	2.00	0.2343	221	0.1603	30	1.37	0.4992	040	0.4518
20	1.99	0.2365	122	0.1610	10	1.425	0.4613	316	0.4606
15	1.96	0.2440	303	0.1684	15	1.415	0.4681	140	0.4612
10	1.935	0.2502	303	0.1720	10	1.40	0.4778	041	0.4614
5	1.89	0.2622	410	0.1775	10	1.40	0.4778	505	0.4677
40	1.855	0.2723	204	0.1890	15	1.415	0.4681	701	0.4681
40	1.84	0.2767	402	0.1892	10	1.40	0.4778	126	0.4681
15	1.815	0.2845	222	0.1894	10	1.383	0.4898	107	0.4772
10	1.76	0.3022	114	0.1916	10	1.383	0.4898	505	0.4776
10	1.75	0.3059	204	0.1922	10	1.383	0.4898	240	0.4893
			313	0.1966	30	1.37	0.4992	406	0.4894
			320	0.1969	25	1.36	0.5061	622	0.4896
			023	0.1991	30	1.31	0.5458	042	0.4901
			313	0.2001	25	1.36	0.5061	241	0.4983
			123	0.2090	10	1.297	0.5572	406	0.4987
			322	0.2341	15	1.260	0.5903	241	0.4991
			223	0.2353	25	1.305	0.5500	425	0.5056
			322	0.2364	10	1.297	0.5572	515	0.5058
			501	0.2439	30	1.31	0.5458	326	0.5453
			510	0.2615	25	1.305	0.5500	341	0.5459
			420	0.2622	10	1.297	0.5572	307	0.5491
			511	0.2720	15	1.260	0.5903	307	0.5573
			421	0.2726	15	1.260	0.5903	127	0.5902
			115	0.2760	10	1.237	0.6125	525	0.5905
			124	0.2763	10	1.237	0.6125	426	0.6116
			323	0.2849	7	1.226	0.6232	516	0.6123
			512	0.3018	7	1.208	0.6417	008	0.6130
			224	0.3019	7	1.208	0.6417	343	0.6237
			422	0.3022	10	1.160	0.6959	244	0.6408
			224	0.3051	20	1.154	0.7034	442	0.6411
			404	0.3057	10	1.160	0.6959	507	0.6955
			215	0.3069	20	1.154	0.7034	705	0.7036
					15	1.150	0.7086	507	0.7094

for hollandite II. The space group was suggested as C_{2h}^5-I4/m , C_4^2-I4 , S_8^2-I4 in the tetragonal system and C_{2h}^3-I2/m , C_2^3-I2 , C_2^3-Im in the monoclinic system, but the structure was derived on the tetragonal basis.

The morphological measurements on a single crystal of hollandite (Fermor's collection No. J 941 from Kajlidongri) with a two circle goniometer give the values,

$$mm'(110 \wedge \bar{1}10) = 89^\circ 42' \pm 12'$$

and

$$ma(110 \wedge 100) = 44^\circ 36' \pm 12'.$$

The rotation and zero-layer Weissenberg photographs (Fe $K\alpha$) about [010] and [100] and equi-inclination 1st and 2nd layer Weissenberg photographs about [010] show the monoclinic symmetry of the crystal with the unit cell

$$a = 10.02, b = 5.76, c = 9.89 \text{ \AA}; \beta = 90^\circ 36'.$$

The weak odd layers in the b axis rotation photographs have also been obtained using Mo $K\alpha$ radiation. The conditions limiting possible reflexions are $h0l$ only with $h+l=2n$, and $0k0$ only with $k=2n$. This indicates the space group $P2_1/n$ (C_{2h}^5). The possibility of centering on the b face was eliminated by taking a rotation photograph about the diagonal axis [101]. The odd layer lines in the rotation photograph with [010] as axis are much weaker than the even layer lines. The cell dimension about [010] appears approximately halved, that is, the molecules repeat approximately at intervals of $b/2$ (Lipson & Cochran, 1953).

The powder spacing data of hollandite (J 941) are almost identical with those reported by Byström & Byström (1950). The indexing with the above cell dimensions is shown in Table 1. The chemical analysis of hollandite (carefully isolated well-developed crystals, J 941) by B. D. Sarma in this laboratory gives in percentage MnO₂ = 65.92, MnO = 5.44, Fe₂O₃ = 12.02, Al₂O₃ = 0.50, BaO = 16.08, H₂O = none, total = 99.96. The spectrum analysis shows traces of Si, K, Pb, Na, Mg, Ca and minute traces of Cu, Ti, Ni, Co, Bi, Sb, Li, Sn, In, Ga

and Ge. The number of atoms in the unit cell per 16 oxygen atoms comes out at Mn⁴⁺ = 6.26, Mn²⁺ = 0.63, Fe = 1.24, Ba = 0.87, Al = 0.08 and the formula may be taken as BaFeMn₇O₁₆, where Mn and Fe are present in different valency states. With the above values of axial lengths and the angle β , ($V = 571 \text{ \AA}^3$), and the density 4.92 g.cm.⁻³ for hollandite (determined for the crystal, J 941), the number of molecules per unit cell comes out to be $Z = 2.03$. The axial lengths and angle determined for a single crystal of hollandite (Museum No. K 302, collected by H. J. Winch from Kajlidongri) are

$$a = 10.03, b = 5.76, c = 9.90 \text{ \AA}; \beta = 90^\circ 42'.$$

The chemical analysis of this hollandite by Winch (1909) gives Mn⁴⁺ = 6.29, Mn²⁺ = 0.60, Fe = 1.10, Ba = 0.96, Al = 0.15 (H₂O nil). With the values of axial lengths and angle β , ($V = 572 \text{ \AA}^3$), and the density 4.94 g.cm.⁻³ (determined for the crystal, K 302) Z comes out to be 2.04.

Byström & Byström observed that all the weak reflexions in the powder photographs of Swedish hollandite II could not be indexed with the same set of crystal elements suggesting the presence of another phase of hollandite in this specimen. It is, however, found possible to index all the reflexions with the same cell reported by Byström & Byström if the b axial length is doubled.

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A preliminary crystallographic investigation of 1-phenylhydantoin and three derivatives of uracil.*

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A preliminary investigation has been made of the crystallographic data of 4-methyl-5-ethyluracil (I), 4-methyluracil-5-acetic acid (II), 4-methyl-5-methylamino-uracil (III), and 1-phenylhydantoin (IV). The lattice constants and space-group data were obtained from rotation and Weissenberg photographs; the determinations were made on the basis of one crystal setting for each species, and the measurements were corrected for

film shrinkage. The angular constants of the direct cells were determined by the method of angular lag (Buerger, 1942): from measurements on (1) an equi-inclination photograph of the first layer in monoclinic cases, (2) a composite anti-equi-inclination photograph (of the zero and first layers, respectively) in triclinic cases. The crystal densities were determined by flotation. The errors are estimated to be about $\pm 0.05 \text{ \AA}$ for the linear constants and about $\pm 0^\circ 20'$ for the angular constants.

(I) $\text{NHCONHC}(\text{CH}_3):\text{C}(\text{C}_2\text{H}_5)\text{CO}$ crystallizes in two

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different habits with two different unit cells according