X-Ray Powder Data and Unit Cell Parameters of $MgBr_2 \cdot 6H_2O$

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Detailed X-ray powder data for $MgBr_2 \cdot 6H_2O$ were obtained by diffractometry by use of CuK_α radiation at 22°C. The data were indexed on a bimolecular monoclinic unit cell, space group C2/m, with a = 10.290 ± 0.001 Å; b = 7.334 ± 0.001 Å; c = 6.211 ± 0.001 Å; β = 93° 25′ ± 10′. Calculated density was 2.074 g/cm^3, compared with a measured density of 2.07 ± 0.01 g/cm^3.

The structure of magnesium bromide hexahydrate, $MgCl_2 \cdot 6H_2O$, was determined by Andress and Gundermann (*1*), who reported a bimolecular unit cell, space group C2/m, with a = 10.25 ± 0.03 Å; b = 7.40 ± 0.03 Å; c = 6.30 ± 0.03 Å; β = 93° 30′ ± 20′. The only available X-ray powder data appeared in the original Hanawalt compilation (*2*) and were subsequently included in the "Powder Diffraction File" (*3*). As was the case with magnesium chloride hexahydrate (*4*), the data are not complete, and calculation of interplanar spacings, by use of the available unit cell parameters, indicates relatively low precision.

X-ray Procedures

Powder data were acquired at 22°C by conventional methods, with a General Electric XRD-700 recording diffractometer with CuK_α radiation generated at 50 kVp and 20 mA. Flat recessed sample holders, machined from

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Table I. X-Ray Powder Diffraction Data for $MgBr_2 \cdot 6H_2O$ at 22°C

hkl	$2\theta_{obs}$	d_{obs}	d_{calc}	I/I_1
001	14.285	6.200_0	6.2000	23
110	14.84	5.969_3	5.9687	1
200	17.265	5.136_0	5.1359	8
$11\bar{1}$	20.29	4.376_6	4.3763	1
111[a]	21.01	4.228_2	4.2274	100
$20\bar{1}$[a]	21.80	4.076_7	4.0763	48
201	23.13	3.845_2	3.8442	2
020[a]	24.270	3.667_1	3.6670	51
021	28.27	3.156_7	3.1563	16
310[a] 002	28.78	3.101_9	3.1025 3.1000	71
220[a]	29.94	2.984_3	2.9844	62
$31\bar{1}$[a]	31.55	2.835_6	2.8365	26
$11\bar{2}$	32.08	2.790_0	2.7909	58
$20\bar{2}$ $22\bar{1}$[a] 311 112	32.92	2.720_7	2.7269 2.7262 2.7164 2.7129	95
221	33.78	2.653_3	2.6534	4
202	34.68	2.586_5	2.5867	2
400	34.94	2.567_9	2.5679	1
$40\bar{1}$[a]	37.085	2.424_4	2.4241	15
130 022[a]	37.96	2.370_2	2.3782 2.3674	19
401[a]	38.745	2.324_3	2.3240	31
$31\bar{2}$	39.99	2.254_5	2.2546	1
$13\bar{1}$	40.43	2.230_9	2.2308	<1
131[a]	40.84	2.209_5	2.2103	16
$22\bar{2}$	41.26	2.188_0	2.1882	2
312	42.31	2.136_1	2.1360	6
222 420[a]	42.94	2.106_2	2.1137 2.1035	68
003	43.80	2.066_8	2.0667	3
$40\bar{2}$	44.47	2.037_2	2.0381	4
$42\bar{1}$	44.81	2.022_5	2.0222	<1
330	45.60	1.989_8	1.9896	7
510[a] $11\bar{3}$	45.96	1.974_6	1.9782 1.9742	6
421 $20\bar{3}$	46.27	1.962_1	1.9630 1.9581	13
113	47.02	1.932_5	1.9323	3
402 $51\bar{1}$ $33\bar{1}$	47.44	1.916_4	1.9221 1.9167 1.9138	24
$13\bar{2}$[a]	47.90	1.899_0	1.8996	25
203 331 132	48.52	1.876_2	1.8789 1.8756 1.8745	24
511	49.14	1.854_0	1.8540	6
040	49.73	1.833_8	1.8335	10
023	50.71	1.800_2	1.8004	6
$42\bar{2}$[a]	51.30	1.780_9	1.7815	14
$31\bar{3}$ 041	51.87	1.762_6	1.7645 1.7582	8
$22\bar{3}$ 240	53.03	1.726_8	1.7273 1.7268	5
$51\bar{2}$ 600[a]	53.52	1.712_1	1.7128 1.7120	8
422 $33\bar{2}$	53.86	1.702_1	1.7024 1.7014	4
313 $60\bar{1}$ 223 $24\bar{1}$[a]	54.89	1.672_6	1.6787 1.6760 1.6722 1.6721	13
$40\bar{3}$ 241	55.43	1.657_6	1.6590 1.6549	2
332	55.76	1.648_5	1.6486	5
512[a] 601	56.60	1.626_0	1.6258 1.6255	4
042 530 $13\bar{3}$[a] 403	58.78	1.570_8	1.5781 1.5728 1.5707 1.5651	7
620 004[a] 133	59.59	1.551_4	1.5512 1.5500 1.5494	10
$53\bar{1}$ $60\bar{2}$	60.04	1.540_8	1.5413 1.5379	10
$62\bar{1}$ $24\bar{2}$	60.85	1.522_3	1.5244 1.5215	2
$11\bar{4}$ $42\bar{3}$ $20\bar{4}$ 531	61.36	1.510_8	1.5130 1.5115 1.5090 1.5082	12
242	62.04	1.495_9	1.4958	2
440 114 621	62.38	1.488_6	1.4922 1.4877 1.4861	30

[a] Lines reported by "Powder Diffraction File," No. 1-1045.

Lucite, were used. Samples containing approximately 20% high-purity rock crystal quartz as an internal standard were scanned from 2° to 63° 2 θ at a rate of 0.2°/min, which permitted measurement of 2 θ values to the nearest 0.01°. Samples containing no internal standard were then scanned, following alignment on the (020) line of the bromide, to provide complete interplanar spacing and intensity data. Integrated intensities were obtained from the diffractometer recording chart by counting squares.

Sample Preparation

All measurements were made with Fisher ACS certified $MgBr_2 \cdot 6H_2O$ crystals. Attempts to grind the crystals to a sufficiently fine powder to obtain reproducible intensities were not successful. The crystals were completely dehydrated, therefore, at 300°C and then allowed to rehydrate at 50°C. After one week at 50°C, the very fine powder was packed in the X-ray sample holder and covered with plastic wrap (Dow Handi-Wrap) to prevent absorption of water during X-ray scanning.

Density Measurements

Densities of rehydrated powder and the crystals were measured by suspension in liquid mixtures at 22°C, as described previously (*4*). Difficulty was encountered in both cases. It proved to be impossible to grind the crystals sufficiently to remove all included air bubbles, and the powder tended to form a static suspension, presumably because of the very small crystallites (approximately 1 μm, as measured by X-ray line broadening).

Results

Measured diffraction angles, 2 θ, interplanar spacings, d_{obs}, and relative intensities, I/I_1, are given in Table I. The indexing procedure used was as described previously (*4*). For the bromide, however, it was necessary to estimate the 2 θ angles of the key lines, (001), (200), (020), (40$\bar{1}$), and (401), to the nearest 0.005° to obtain acceptable agreement between calculated and observed interplanar spacings. The revised lattice parameters are a = 10.290 ± 0.001 Å; b = 7.334 ± 0.001 Å; c = 6.211 ± 0.001 Å; β = 93° 25′ ± 10′.

Indexing is in agreement with the reported space group, C2/m, in that $h + k = 2n$ for all lines. The unit cell volume is 467.89 Å^3, and the calculated density, ρ_x, is 2.074 g/cm^3. The best value that can be placed on the measured density is 2.07 ± 0.01 g/cm^3, in agreement with the calculated value and considerably higher than that obtained from the X-ray data of Andress and Gundermann (*1*), 2.035, or that reported in the "Handbook of Chemistry and Physics" (*5*), 2.00.

Literature Cited

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Vapor Pressure of Methanol from 288.15 to 337.65K

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Forty-two measurements of the vapor pressure of methanol are made at 5K intervals from 288.15 to 337.65K with a new static vapor-pressure apparatus. The estimated uncertainties in the experimental temperature and pressure are ±0.002K and ±1 Pa, respectively. The measurements are represented by the equation: $\ln(P/\mathrm{kPa}) = 15.76129944 - 2.845920984 \times 10^3\, K/T - 3.743415457 \times 10^5\, K^2/T^2 + 2.188669828 \times 10^7\, K^3/T^3$. This equation is compared with the best previous measurements, with agreement generally within the experimental uncertainties reported by other workers.

As part of a study of the vapor pressures of solutions of several nonvolatile solutes in methanol (*4*), we have measured the vapor pressure of pure methanol. The methanol used was of the highest purity; it contained less than 0.005 mol % water and even less of any other volatile impurity. Our new static vapor-pressure apparatus operates with a precision of ±0.002K in the temperature (temperatures in this paper are expressed as International Practical Kelvin Temperatures T_{68}, which for most purposes are indistinguishable from thermodynamic temperatures T) and ±1 Pa in the pressure. No previous measurements of this precision have been reported for methanol.

Materials

The methanol used as a starting material was Fisher certified reagent grade, rated by the manufacturer as 99.9 mol % pure. This material was distilled through a 1-m vacuum-jacketed column filled with 0.6-cm glass helices into a degassing apparatus similar to that of Taylor (*15*). This methanol contained less than 0.001 wt % water by Karl Fischer titration (*9*) and less than 0.003% acetone and formaldehyde by the test of Morton and Mark (*10*). A second batch of methanol, prepared by addition of potassium hydroxide and dimethyl phthalate to methanol and distillation of the mixture, contained 0.025 wt % water.

Apparatus

The static vapor-pressure apparatus contains an oil thermostat, regulated at ±0.001K, for the vapor-pressure cell, and an air thermostat, regulated to ±0.01K, for the null manometer. The vapor-pressure cell is similar to the one used by Scatchard et al. (*13*); it is fitted with the de-

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