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On the Crystal Structures of $RbCoCl_3$ and Rb_3CoCl_5

Å. ENGBERG and H. SOLING

The Chemical Laboratory B, Technical University of Denmark, Kgs. Lyngby, Denmark

The crystal structures of the compounds $RbCoCl_3$ and Rb_3CoCl_5 have been investigated by means of their X-ray powder patterns.

$RbCoCl_3$ crystallizes in the hexagonal system with the space group $P6_3/mmc$ and lattice constants $a_H = 6.999$ Å $\pm$ 0.001, $c_H = 5.996$ Å $\pm$ 0.001. The main feature of the structure is the infinite chains of $CoCl_6$-octahedra sharing faces in the c_H-direction, as has been found also in $CsNiCl_3$. The otherwise quite straightforward analysis has been somewhat hindered by a systematic irregularity in the observed intensities, which eventually was interpreted as a structural disorder in the samples investigated.

Rb_3CoCl_5 crystallizes in the tetragonal system with the space group $I4/mcm$ and the lattice constants $a = 8.799$ Å $\pm$ 0.001, $c = 14.239$ Å $\pm$ 0.002. A comparison with the intensity data for the known structure of Cs_3CoCl_5 gives strong evidence of the isomorphism of the two compounds.

A differential thermal analysis by Seifert [1] of the system $RbCl$-$CoCl_2$ has demonstrated the existence of the compounds $RbCoCl_3$, Rb_2CoCl_4, and Rb_3CoCl_5. The thermogram suggests that Rb_2CoCl_4 is di-morphous. Previously only Rb_3CoCl_5 and the dihydrates of the two other compounds were known.[2] The knowledge about the crystal structures is scarce. Seifert [1] states that $RbCoCl_3$ and α-Rb_2CoCl_4 are isomorphous with $CsNiCl_3$ [3] and Cs_2CoCl_4 [4] respectively, but gives no details. From a single oscillation photograph of Rb_3CoCl_5 Powell and Wells [5] deduce the tetragonal axes $a = 8.7$ Å and $c = 14.0$ Å. The present paper reports some results obtained from X-ray powder photographs of $RbCoCl_3$ and Rb_3CoCl_5.

1. THE CRYSTAL STRUCTURE OF $RbCoCl_3$

Polycrystalline samples of $RbCoCl_3$ were prepared both by gently dehydrating powdered $RbCoCl_3.2H_2O$ at room temperature, and by melting together in an atmosphere of dry HCl at 600°C a stoichiometric mixture of $CoCl_2$ and RbCl. The preparations were controlled by chemical analyses (Co and Cl). $RbCoCl_3$ is blue and very hygroscopic. The brittle crystals show two predominating directions of cleavage which are mutually perpendicular. The

Table 1. Observed and calculated $1/d^2$ and intensities for $RbCoCl_3$.

hk l	$1/d^2$ calc.*	$1/d^2$ obs.	*I* calc.	*I* obs.
10 1	0.0554	0.0553	200	268
11 0	0.0822	0.0822	542	685
20 0	0.1095	0.1095	83	444
00 2	0.1118	0.1117	280	
20 1	0.1373	0.1372	2168	2333
10 2	0.1391	0.1390	403	
21 0	0.1912	0.1914	33	25
11 2	0.1936		10	
21 1	0.2191	0.2208	140	1191
20 2	0.2209		1197	
30 0	0.2458	0.2457	262	340
30 1	0.2736	—	10	25
10 3	0.2783	0.2781	56	
21 2	0.3027	0.3025	585	596
22 0	0.3275	0.3274	1041	1013
31 0	0.3548	0.3553	38	
30 2	0.3572	0.3604	4	732
20 3	0.3602		750	
31 1	0.3827	0.3828	128	186
40 0	0.4365	0.4391	20	450
22 2	0.4389		422	
21 3	0.4419	0.4459	48	280
00 4	0.4460		219	
40 1	0.4643	0.4642	619	943
31 2	0.4661		272	
10 4	0.4732	—	43	25
30 3	0.4963	—	5	25
32 0	0.5182	0.5189	47	109
11 4	0.5276	0.5277	174	194
32 1	0.5460	0.5477	120	720
40 2	0.5478		456	
20 4	0.5541	—	22	25
41 0	0.5726	0.5724	238	238
41 1	0.6004	—	9	25
31 3	0.6052	0.6047	65	25
32 2	0.6294	0.6298	147	166
21 4	0.6366	—	31	94
50 0	0.6814	—	1	25
41 2	0.6838	—	1	
40 3	0.6867	0.6868	493	611
30 4	0.6909	—	155	
50 1	0.7092	—	20	25
10 5	0.7235	—	14	60
33 0	0.7357	0.7362	124	134
42 0	0.7629	—	40	
32 3	0.7683	0.7722	92	1231
22 4	0.7724		1134	
42 1	0.7907		1211	
50 2	0.7924	0.7905	213	1544
31 4	0.7996		68	
20 5	0.8048	0.8043	492	412
41 3	0.8226	—	11	25

* Corrected for absorption.

51 0	0.8443	—	6	25
33 2	0.8467	—	0	25
51 1	0.8720 }		97 }	
42 2	0.8738 }	0.8736	1131 }	1067
40 4	0.8809 }		37 }	
21 5	0.8863	—	18	25
50 3	0.9312	—	17	25
30 5	0.9407	—	8	25
51 2	0.9554 }	0.9556	520 }	626
32 4	0.9626 }		194 }	
60 0	0.9803	0.9803	1218	1268
00 6	1.0016	—	100	25
43 0	1.0073	—	1	25
60 1	1.0080	—	0	25
42 3	1.0127	1.0126	2684 }	3435
41 4	1.0168	1.0168	824 }	

crystals are optically positive and uniaxial. The main direction of cleavage is parallel to the optical axis.

The dimensions of the hexagonal unit cell determined from powder-patterns are:

$$a_H = 6.999 \text{ Å} \pm 0.001 \text{ and } c_H = 5.996 \text{ Å} \pm 0.001$$

(Fe$K\alpha$-radiation; 19 cm Bradley-Jay camera, calibrated with NaCl). The lattice parameters were corrected for absorption by extrapolation, according to Nelson and Riley.[6] The observed and calculated d-spacings are collected in Table 1.

The Friedel symmetry $6/mmm$ as well as the space group extinctions, $hh \cdot l$ absent for $l = 2n + 1$, were observed by means of Weissenberg $hk0$, $hk1$ and $hk2$ photographs (Mo$K\alpha$-radiation), which lead to the possible space groups: $P6_3/mmc$ $P\bar{6}2c$ and $P6_3mc$. The observed density 3.24 g·cm^{-3} corresponds with two formula units per unit cell.

Since no single crystals suitable for quantitative work could be found in the several preparations, it was decided to attempt a structure analysis by means of the powder data. The integrated intensities of the powder lines were measured with a photometer (Schnellphotometer III, Zeiss, Jena) and compared with those calculated by standard procedures. The applied scattering factors, corrected for anomalous scattering, were those given by Cromer [7] and by Cromer and Waber.[8] The correction for absorption was based upon the assumption that the sample could be considered a homogeneous cylinder.

Geometrical considerations suggest a structure based upon a hexagonal close packing (h) of layers of the composition $RbCl_3$, with Co^{2+}-ions in 1/4 of the octahedral interstices. Specifically, the following special positions in space-group $P6_3/mmc$ were used as a trial structure.

2 Co in a: (0,0,0) *etc.*
2 Rb in d: (1/3, 2/3, 3/4) *etc.*
6 Cl in h: $(x, \bar{x}, 1/4)$ *etc.* $x \sim 1/6$.

Comparison of the observed intensities with the intensities calculated on this basis revealed that the ratios $I_c(hkl)/I_o(hkl)$ were systematically higher for the reflexions with $l \neq 0$ than for those with $l = 0$. This systematic irregularity may be accounted for by a suitable change in the z-parameter of the Rb^+-ion, (Space group $P6_3mc$, pos. b). In view of the relative sizes of the Rb^+-ion and the Cl^--ion deviations from the ideal hexagonal packing of these ions are expected. The results of our analysis based on the space group symmetry $P6_3mc$ have been published in a preliminary report.[9] Later investigations, however, have shown that the systematic irregularity in the I_c/I_o-values is strongly dependent on the previous treatment of the powder. In fact it can be considerably reduced, although not completely removed, from all our samples by a rather protracted heat treatment. For practical reasons the heat treatment was confined to 72 h at 300°C.

This experience suggests a disorder in the lattice, rather than preferred orientation in the sample, as was suspected at first. Hence the above mentioned considerations concerning the packing of the Rb^+-ions with the Cl^--ions may still be relevant, albeit now in a statistical sense. Mathematically this may be expressed by introducing an anisotropic temperature factor of the form:[10]

$$f_T'(\text{Rb}) = f_T(\text{Rb}) \times \exp(-B'\cdot\cos^2 \varphi \cdot \sin^2 \theta/\lambda^2)$$

where φ is the angle between the direction of the displacement and the normal to the reflecting plane.

The original model based upon the space group $P6_3/mmc$ was now reassumed, and the set of observed intensities, which showed the smallest systematic irregularity in the intensity ratios was compared with several sets of calculated intensities. The fit of the data was conventionally expressed in terms of the R-index:

$$R = \sum|I_o - I_c|/\sum I_o$$

where the non-observed intensities were put equal to half the minimum observable value.

In the first series of calculations B' in the expression for $f_T'(\text{Rb})$ was put equal to zero and a minimum value of R as a function of x was searched in the interval $0.152 < x < 0.167$. We found $R_{\min} = 0.14$ for $x = 0.160$. The overall temperature factor B was 2.6 Å^2. Then the correction for the anisotropy of the Rb^+-ion was introduced, and a new systematic minimization was undertaken by varying both B', B and x in turn. We found $R_{\min} = 0.108$ when $B' = 2.0$ Å^2, $B = 2.3$ Å^2, and $x = 0.161$. The calculated and observed intensities are collected in Table 1.

During the progress of the calculations it turned out that the value of the x(Cl)-parameter is only slightly dependent upon the values of B' and B. Finally the x(Cl)-value was controlled by minimizing $R' = \sum(I_o - I_c)^2 \times w$ with respect to x(Cl) only. An empirical weighting scheme $\sqrt{w} = 1/\sigma(I_o - I_c)$, where $\sigma(I_o - I_c) = I_o(\min) + 0.05\ I_o(hkl)$ was employed. Non-observed reflexions were given zero weight. We found $x(\text{Cl}) = 0.161 \pm 0.002$.

For the sake of completeness it should be added that attempts to gain another free parameter by replacing the 6_3-axis by a $\bar{6}$-axis (space group $P\bar{6}2c$) have proved incompatible with the observed intensities.

The analysis shows that the structure type is of the $CsNiCl_3$-type,[3] which has also been found for several other double halides of Co and Ni being investigated in this laboratory. The characteristic feature of this structure is the infinite chains of slightly deformed $CoCl_6$-octahedra sharing faces as shown in Fig 1. The interatomic distances and angles found are listed in Table 2. The distance between Cl-atoms situated on a shared face is considerably shorter than the distance between Cl-atoms on a non-shared face, which in turn is only a trifle shorter than two ionic radii.

Table 2. Interatomic distances and angles in $RbCoCl_3$.

Cl(1) – Cl(2) = 3.38 Å ± 0.04	Co – Cl = 2.46 Å ± 0.02
Cl(1) – Cl(3) = 3.577 Å ± 0.013	Co – Co = $\frac{1}{2}$ c_H = 2.998 Å ± 0.001
Rb(1) – Cl(1) = 3.504 Å ± 0.001	∠Cl(1)–Co–Cl(3) = 93.3° ± 0.5°
Rb(2) – Cl(2) = 3.655 Å ± 0.014	∠Cl(1)–Co–Cl(2) = 86.7° ± 0.5°

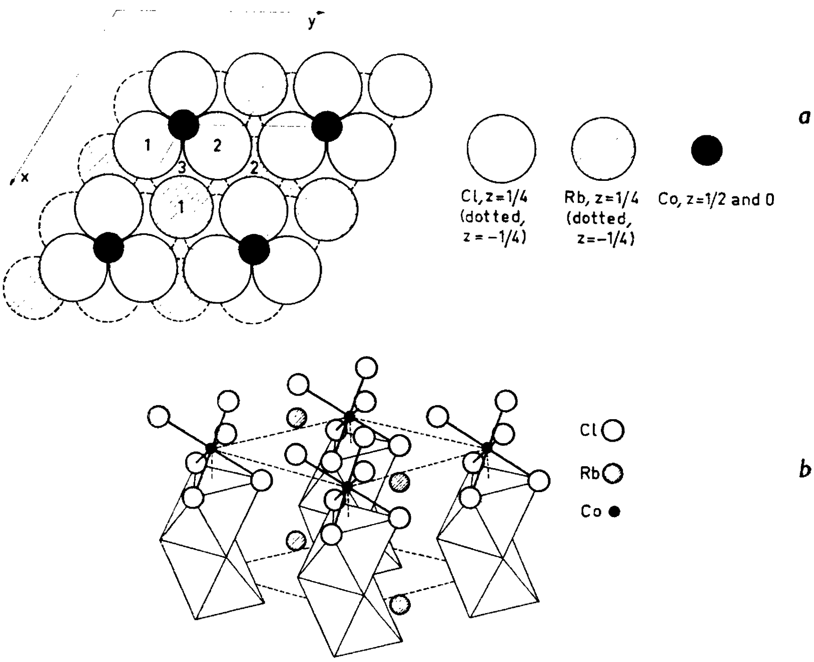

Fig. 1. The crystal structure of $RbCoCl_3$. a) Projection on the x-y plane. b) Atomic arrangement and packing of coordination octahedra.

2. THE CRYSTAL STRUCTURE OF Rb_3CoCl_5

A polycrystalline sample of Rb_3CoCl_5 was prepared from RbCl and $CoCl_2$ by melting a stoichiometric mixture of the component salts in an atmosphere of dry HCl at 600°C. The blue substance is not hygroscopic. The crystals are optically positive and uniaxial, without any marked direction of cleavage.

Table 3. Observed and calculated $1/d^2$ for Rb_3CoCl_5. Powder line intensities for Rb_3CoCl_5 and Cs_3CoCl_5.

hkl	$1/d^2$ obs.	$1/d^2$ calc.*	*I* obs. Rb_3CoCl_5	*I* obs. Cs_3CoCl_5
211	0.0701	0.0701	1	1
202	0.0722	0.0721	4	4
004	0.0795	0.0796	2	2
220	0.1041	0.1041	3	2
213	0.1097	0.1098	5	5
310	0.1299	0.1300	4	4
312	0.1496	0.1498	1	n.o.
006	0.1783	0.1785	½ }	3
224	0.1833	0.1831	3 }	
215	0.1889	0.1889	2	2
116	0.2048	0.2044	½ }	3
314	0.2090	0.2091	1 }	
323	0.2130	0.2133	½	n.o.
411	0.2256	0.2255	½	n.o.
402	0.2273	0.2274	½	3
206	0.2303	0.2302	3	3
330	0.2337	0.2335	2	1
332	0.2531	0.2532	1	2
420	0.2593	0.2593	3	3
413	0.2648	0.2649	3	3
422	0.2788	0.2790	1	½
404	0.2866	0.2866	2	1
316	0.3077	0.3077	3	2
008	0.3166	0.3166	2	1
424	0.3382	0.3382	3	2
415	0.3434	0.3439	1	1
406	0.3852	0.3851	3	2
336	0.4109	0.4109	1	}
440	0.4142	0.4141	1	1 } 4
523 (228)	0.4189	0.4197 (0.4198)	4	}
318	0.4455	0.4455	1	n.o.
600	0.4653	0.4656	4	3
444	0.4925	0.4928	½	½
525	0.4984	0.4984	½	½
534	0.5184	0.5186	2	2
622	0.5369	0.5368	2	2
604	0.5445	0.5444	3	2
543 (428)	0.5741	0.5743 (0.5743)	4	2+2 (428)
419	0.6194	0.6194	2	½
21 11	0.6615	0.6616	1	3 (+642)
626	0.6942	0.6943	3	2
00 12	0.7101	0.7103	1	}
723 (448)	0.7288	0.7290 (0.7290)	2	n.o. } 3
644 (730)	0.7501	0.7506 (0.7492)	3	}
529	0.7748	0.7741	2 }	4
608	0.7807	0.7807	3 }	
31 12	0.8395	0.8394	½	}
646	0.8494	0.8491	3	2 } 2
820	0.8781	0.8782	½	}

n.o. = not observed.
* corrected for absorption.

813	0.8839	0.8839	2	2
736	0.9266	0.9266	2	n.o.
660	0.9297	0.9299	2	1
33 12	0.9429	0.9427	1	n.o.
824	0.9572	0.9571	2	1
815	0.9628	0.9628	2	1
42 12	0.9687	0.9685	1	4 (+648)
664 (62 10)	1.0093	1.0088 (1.0098)	½	2 (+840−664)
20 14	1.0185	1.0183	½	½ (+835)

The X-ray powder-pattern could be indexed tetragonally as shown in Table 3. (Fe$K\alpha$-radiation, 19 cm Bradley-Jay-camera). The lattice constants found by extrapolation [6] are

$$a = 8.799 \text{ Å} \pm 0.001, c = 14.239 \text{ Å} \pm 0.002, c/a = 1.618$$

The observed density 2.99 g·cm^{-3} corresponds with 4 Rb_3CoCl_5 per unit cell.

The systematically absent reflexions agree with the space groups $I4cm$, $I\bar{4}c2$, and $I4/mcm$. The crystals do not show any detectable piezoelectric effect, so the centrosymmetric space group $I4/mcm$ is considered the most probable.

The crystal structure of Cs_3CoCl_5 has recently been refined by Figgis, Gerloch and Mason;[11] they find the tetragonal axes a = 9.219 Å ± 0.003 and c = 14.239 Å ± 0.005, c/a = 1.579; space group $I4/mcm$.

Powder diagrams of the two compounds were photometered and the scaled intensities were compared as shown in Table 3, columns 4 and 5. From the very close similarity in the intensities we conclude that Rb_3CoCl_5 and Cs_3CoCl_5 are isomorphous.

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