SPACE GROUP OF THE ROOM TEMPERATURE FORMS OF CAESIUM AND RUBIDIUM NITRATES

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Infrared and Raman studies[1,2] on room temperature forms of both caesium and rubidium nitrates are almost identical, indicating similar site group symmetries. However, different space groups have been determined from X-ray diffraction measurements. They were reported to be $P31m$ (C_{3v}^2), $a = 1087$, $c = 776$ pm, for caesium nitrate [phase II],[3] and $P3_112$ (D_3^3) or $P3_212$ (D_3^5), $a = 1048$, $c = 745$ pm, for rubidium nitrate [phase IV].[4]

Two interesting results emerged from an analysis of full three-dimensional single crystal neutron data of caesium nitrate. The data were collected in one sextant on a spherical crystal (diameter 5 mm, $\mu = 0{\cdot}21$ cm^{-1}), using the single crystal diffractometer of the Australian Institute for Nuclear Science and Engineering installed on the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights, New South Wales:

(1) Because only the $l = 3n$ type reflections are present for ($00l$) values, a threefold screw axis in the c direction is indicated.

(2) The structure amplitudes for (hkl) reflections are significantly different from those for the (khl) type (Table 1), indicating that the Laue group is $\bar{3}$, rather than $\bar{3}m$ which was previously reported.[3] Therefore, the space group is either $P3_1$ (C_3^2) or its enantiomorph $P3_2$ (C_3^3).

The difference in intensities is considered to be real and not due to misorientation of the crystal [$I(200) = I(020) = I(\bar{2}00) = I(0\bar{2}0)$].

Neutron powder spectra (Table 2) of the room temperature forms of both caesium and rubidium nitrates were similar, indicating that the compounds were isomorphous. The samples were contained in a vanadium can mounted on a neutron powder diffractometer.

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TABLE I

COMPARISON OF (hkl) WITH (khl) TYPE REFLECTIONS

Statistical error of F_{obs} is estimated to be within 1%

h	k	F_{obs} hkl	F_{obs} khl	F_{obs} $hk\bar{l}$	F_{obs} $kh\bar{l}$
			$l = 0$		
1	2	228	226		
1	3	204	393		
1	4	205	201		
1	5	230	224		
1	6	154	329		
1	7	154	156		
1	8	364	290		
1	10	365	369		
2	3	374	483		
2	4	380	380		
2	6	213	277		
2	7	248	252		
2	8	315	323		
2	9	239	313		
3	4	268	227		
3	5	311	234		
3	7	363	254		
4	5	315	325		
4	6	353	478		
4	7	394	400		
4	8	207	289		
5	6	372	419		
5	7	88	106		
			$l = 1$		
1	2	368	268	184	240
1	3	548	416	352	418
1	4	447	376	517	514
1	5	239	179	329	482
1	6	279	223	233	173
1	7	487	413	223	233
1	8	390	329	287	376
1	9	364	252	318	329
2	3	254	224	237	186
2	4	63	162	299	223
2	6	316	310	295	206
2	7	260	484	387	283
2	8	377	356	290	216
3	5	315	297	374	421
3	6	417	411	320	322
3	7	216	246	320	310
4	5	290	190	302	347
			$l = 2$		
1	2	142	188	377	359
1	3	461	373	154	153
1	4	280	289	361	352
1	5	232	305	297	176
1	6	166	191	290	201
1	7	270	278	830	752
1	8	527	445	381	443
1	9	219	208	372	250
2	3	311	232	260	169
2	5	1404	1327	261	287
2	6	484	369	436	435
2	7	518	396	411	456
2	8	694	576	352	291
3	4	267	262	264	278
3	5	461	614	222	220
3	8	517	675	362	363
4	5	141	196	399	293
4	7	458	442	1172	1071
			$l = 3$		
1	2	262	252	174	170
1	3	244	303	271	278
1	4	383	384	286	383
1	5	273	218	292	288
2	5	398	382	387	367
2	6	241	248	98	132
3	4	629	490	361	209
3	6	113	220	285	302
4	5	191	186	251	239
5	6	252	337	322	413
			$l = 4$		
1	2	368	327	148	210
1	3	291	235	323	326
1	5	622	527	272	336
1	6	192	153	402	392
1	7	426	323	434	442
1	8	729	418	146	180
2	3	300	361	324	297
2	5	205	197	694	659
2	7	353	635	470	311
3	5	119	107	224	365
3	6	417	412	321	312
4	6	204	114	394	401
			$l = 5$		
1	2	325	348	210	183
1	3	304	284	261	157
1	4	135	133	249	170
1	5	299	354	372	340
2	3	517	437	268	260
2	4	182	110	90	102
2	5	261	298	279	276
2	6	563	430	126	144
2	7	345	261	113	205
3	4	111	112	245	296
3	6	242	227	379	373
			$l = 6$		
1	2	327	319	391	382
1	4	364	329	252	239
2	3	375	435	349	402
2	4	283	266	525	503
2	5	265	250	276	262
3	4	667	526	401	382
3	6	513	420	454	427
			$l = 7$		
1	2	371	301	335	367
1	4	581	525	201	273

Cell dimensions, determined from the neutron data, found for $CsNO_3$, $a = 1092 \pm 4$, $c = 777 \pm 2$ pm; and $RbNO_3$, $a = 1051 \pm 3$, $c = 747 \pm 2$ pm. The wavelength used was 108·3 pm.

TABLE 2

NEUTRON POWDER SPECTRA OF CAESIUM AND RUBIDIUM NITRATE

hkl	111	021	030	221	032	041	222	141	330	252
$CsNO_3$: d_{hkl} (pm)	446	404	315	258	245	226	223	200	182	141
I	57	5	100	7	10	20	50	15	27	33
$RbNO_3$: d_{hkl} (pm)	430	389	303	247	235	217	215	192	175	135
I	55	5	100	7	10	17	42	12	22	35

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