

The Crystal Structure of Ce_2Ni_7 *

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The structure determination of Ce_2Ni_7 is described. The unit cell is hexagonal, probable space group $P6_3/mmc$, with $a = 4.98 \pm 0.02$, $c = 24.52 \pm 0.08$ Å, and contains four formula units. The structure consists of double layers of the CeNi_5 structure (CaCu_5 type) alternating with double layers of the CeNi_2 structure (Cu_2Mg type). Relationships between this structure, the CeNi_3 , and PuNi_3 structures, the fundamental MX_5 structure and the three Laves or Friauf phases are discussed in detail.

Introduction

Vogel (1947), in a study of the cerium–nickel phase diagram, reported the six compounds Ce_3Ni , CeNi , CeNi_2 , CeNi_3 (?), CeNi_4 (?) and CeNi_5 . The exact compositions of the compounds listed as CeNi_3 and CeNi_4 were uncertain. The crystal structures of CeNi_3 and PuNi_3 were recently reported by Cromer & Olsen (1959) so that the uncertainty with regard to the composition CeNi_3 no longer exists. In that paper it was noted that an unknown compound was found in the specimen from which the CeNi_3 crystals had been obtained. This unknown compound has now been identified as Ce_2Ni_7 . Unless there are more than six compounds in the cerium–nickel system, the compound for which Vogel (1947) suggested the composition CeNi_4 is, in reality, Ce_2Ni_7 .

Experimental

The method of preparation of the cerium–nickel alloy has already been given by Cromer & Olsen (1959). About twenty fragments from this alloy were examined by X-rays. Only one single crystal of Ce_2Ni_7 was found, the other fragments being single crystals of CeNi_3 , or multiple, unidentified crystals. The unit cell of Ce_2Ni_7 is hexagonal with $a = 4.98 \pm 0.02$ and $c = 24.52 \pm 0.08$ Å, as determined from precession photographs ($\text{Mo } K\alpha \lambda = 0.7107$ Å). The classes of reflection $00l$ and hhl were observed to be absent with l odd. Also, hkl reflections where $h - k = 3n$ were absent with l odd. These extinctions are characteristic of space group $P6_3/mmc$ or the non-centric $P6_2c$.

For intensity measurements a series of timed Weissenberg photographs of the $h0l$ layer was made with $\text{Mo } K\alpha$ radiation. The crystal had the approximate dimensions $0.070 \times 0.025 \times 0.010$ mm., and the longest dimension made an angle of about 15° with the rotation axis. Intensities were estimated by visual comparison with a series of spots of known relative intensity made by reflections from the same crystal. Intensities were recorded to $\sin \theta / \lambda = 1.223$. Within this range, 189 reflections out of a possible 503 were

observed to be greater than zero. The calculated density with four formula units per unit cell is 8.55 g.cm.^{-3} .

Determination of the structure

Having only one small crystal to work with, and not knowing its exact chemical composition or density, the authors had to base their speculation as to the identity of the compound on volume considerations and the $h0l$ Patterson projection. The cerium and nickel atomic volumes were derived from CeNi_2 and CeNi_5 , and are 22.6 and 12.0 Å³, respectively. The unit-cell volume observed for the new compound is 524 Å³. The volume calculated for 9 CeNi_3 is 527 Å³. (This unit cell has essentially the same size as that of the non-primitive hexagonal cell of PuNi_3 containing nine formula units.) The compound could hardly be a polymorphic form of CeNi_3 since it had been found in the same alloy in which CeNi_3 had been found. No integral number of CeNi_4 formula units agrees with the observed cell volume. It was therefore necessary to consider other compositions. The most likely unit cell content seemed to be 4 Ce_2Ni_7 having a calculated volume of 517 Å³. This unit cell would also contain even numbers of each kind of atom, which is a requirement of the space groups indicated by the

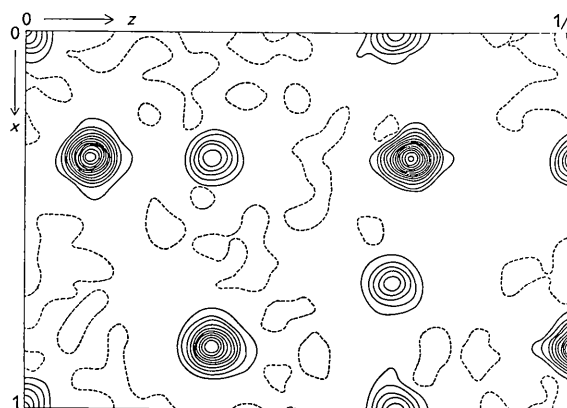


Fig. 1. Fourier projection of Ce_2Ni_7 on a plane normal to the b axis. The dashed contour is at $\rho = 0$. The contour interval is $20 \text{ e.}\text{Å}^{-2}$.

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Table 1. Final parameters of Ce₂Ni₇ from the least-squares refinement

Atom	x	z	B × 10 ¹⁶ cm. ²
Ni ₁	0	0	0.50 ± 0.21
Ni ₂	0	0.1670 ± 0.0004	0.64 ± 0.16
Ni ₃	‡	0.8334 ± 0.0004	0.60 ± 0.14
Ni ₄	0.8351 ± 0.0018	‡	0.41 ± 0.08
Ni ₅	0.8338 ± 0.0014	‡	0.67 ± 0.07
Ce ₁	‡	0.0302 ± 0.0002	0.62 ± 0.07
Ce ₂	‡	0.1747 ± 0.0002	0.61 ± 0.06

systematic extinctions. The CeNi₃ structure had been found to consist of alternating single layers of CeNi₅ and double layers of CeNi₂. If another layer of CeNi₅ were to be inserted in the CeNi₃ structure, so that double layers of CeNi₅ alternated with double layers of CeNi₂, the composition Ce₂Ni₇ would be attained. These two extra layers in the unit cell would add about 8 Å to the c axis of CeNi₃ making c for the postulated Ce₂Ni₇ about 24.5 Å, in agreement with the observed value. A structure of this nature was found to be both

qualitatively and quantitatively in agreement with the *hOl* Patterson projection.

This trial structure had atoms in the following positions of space group *P6₃/mmc*:

- 2 Ni₁ in *a*: 0, 0, 0; 0, 0, $\frac{1}{2}$
 4 Ni₂ in *e*: 0, 0, *z*, etc., $z \approx \frac{7}{8}$
 4 Ni₃ in *f*: $\frac{1}{3}$, $\frac{2}{3}$, *z*, etc., $z \approx \frac{5}{8}$
 6 Ni₄ in *h*: *x*, 2*x*, $\frac{1}{2}$, etc., $x \approx \frac{5}{8}$
 12 Ni₅ in *k*: *x*, 2*x*, *z*, etc., $x \approx \frac{1}{8}$, $z \approx \frac{1}{2}$
 4 Ce₁ in *f*: $\frac{1}{3}$, $\frac{2}{3}$, *z*, etc., $z \approx 0.03$
 4 Ce₂ in *f*: $\frac{1}{3}$, $\frac{2}{3}$, *z*, etc., $z \approx \frac{1}{8}$

The trial structure was refined by the least-squares method. Seven position parameters, seven isotropic temperature factors and the scale factor were simultaneously refined. The complete 15 × 15 matrix was solved for parameter shifts and inverted for standard deviation calculations. Cerium form factors were taken

Table 2. Calculated and observed structure factors for Ce₂Ni₇

The column headings are *h*, *l*, *F_o* and *F_c*. The minus sign for an *F_o* should be interpreted as 'less than'. If *F_o* = 0, the reflection was obscured by the beam trap

<i>h</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
0	2	0	15	1	32	-36	9	2	34	57	-62	3	37	-43	2
1	33	66	54	2	35	-40	32	3	38	-43	-2	4	43	-46	43
0	4	0	24	1	34	62	-53	2	36	-41	-46	3	39	-44	-1
0	6	86	86	1	35	98	-93	2	37	112	111	3	40	72	56
0	8	188	-162	1	36	50	26	2	38	-42	24	3	41	-45	1
0	10	70	-75	1	37	-41	-0	2	39	-43	14	3	42	-45	43
0	12	521	562	1	38	-41	0	2	40	-43	-16	3	43	-46	-2
0	14	335	-348	1	39	-42	7	2	41	123	124	3	44	-46	-54
0	16	158	-158	1	40	-43	-28	2	42	91	76	3	45	-46	1
0	18	154	-157	1	41	89	-88	2	43	-45	-49	3	46	-46	-1
0	20	185	-200	1	42	-44	22	2	44	-45	6	3	47	-46	-1
0	22	-28	11	1	43	-44	-45	2	45	-46	-9	3	48	-46	-41
0	24	352	326	1	44	-45	30	2	46	-46	3	3	49	-45	2
0	26	124	-133	1	45	-45	-3	2	47	-46	38	3	50	-45	-30
0	28	71	77	1	46	-46	5	2	48	-46	15	3	51	-44	-1
0	30	-34	11	1	47	81	-70	2	49	-46	38	3	52	-44	-2
0	32	52	34	1	48	47	60	2	50	-46	37	3	53	-43	-1
0	34	150	143	1	49	-46	39	2	51	-45	-18	3	54	-42	4
0	36	255	217	1	50	-46	17	2	52	-45	11	3	55	-41	-1
0	38	59	-54	1	51	-46	25	2	53	-44	36	3	56	-40	-17
0	40	53	43	1	52	-45	5	2	54	70	59	3	57	-38	1
0	42	55	-67	1	53	-45	-15	2	55	92	-88	4	0	175	-166
0	44	-46	-15	1	54	-44	27	2	56	-41	-9	4	1	192	-189
0	46	-46	16	1	55	-43	28	2	57	-40	-27	4	2	-28	-3
0	48	-46	43	1	56	-42	10	2	58	-39	-6	4	3	83	-97
0	50	74	-78	1	57	-41	26	2	59	-38	-5	4	4	-29	-8
0	52	-45	-16	1	58	-40	-2	3	0	333	328	4	5	171	-158
0	54	45	-66	1	59	-39	-11	3	1	-23	5	4	6	73	77
0	56	-43	19	1	60	-37	24	3	2	-24	18	4	7	-29	-13
0	58	-41	21	2	0	265	-265	3	3	-24	-2	4	8	43	41
0	60	55	52	2	1	324	303	3	4	25	26	4	9	-30	4
1	0	30	-32	2	2	20	-6	3	5	-24	5	4	10	31	25
1	1	27	-35	3	3	147	154	3	6	421	408	4	11	31	33
1	2	14	-14	2	4	-19	-9	3	7	-25	-5	4	12	50	-59
1	3	25	-26	2	5	290	256	3	8	142	-127	4	13	227	-222
1	4	20	-17	2	6	147	131	3	9	-25	2	4	14	92	105
1	5	16	-11	2	7	-20	7	3	10	66	-70	4	15	-36	-12
1	6	108	-108	2	8	62	63	3	11	-26	-4	4	16	47	50
1	7	322	-323	2	9	-21	-14	3	12	73	71	4	17	80	-86
1	8	104	91	2	10	32	34	3	13	-27	4	4	18	69	130
1	9	119	-116	2	11	57	-51	3	14	203	-215	4	19	111	102
1	10	55	53	2	12	80	-89	3	15	-28	-2	4	20	62	67
1	11	204	-168	2	13	357	319	3	16	79	-89	4	21	140	145
1	12	120	115	2	14	143	146	3	17	-29	3	4	22	-36	-1
1	13	85	-91	2	15	26	24	3	18	170	137	4	23	79	92
1	14	135	141	2	16	68	70	3	19	-31	-4	4	24	47	-43
1	15	71	74	2	17	122	122	3	20	199	-199	4	25	61	-58
1	16	60	62	2	18	159	181	3	21	-32	2	4	26	39	47
1	17	25	27	2	19	144	-144	3	22	34	-19	4	27	63	84
1	18	32	34	2	20	78	87	3	23	-33	-3	4	28	-39	-27
1	19	46	-62	2	21	165	-193	3	24	49	53	4	29	58	-50
1	20	107	121	2	22	-30	-0	3	25	-35	3	4	30	42	51
1	21	127	137	2	23	110	-118	3	26	63	-64	4	31	99	93
1	22	-28	16	2	24	46	-57	3	27	-36	-1	4	32	-42	-14
1	23	-29	11	2	25	70	76	3	28	84	92	4	33	75	66
1	24	62	66	2	26	59	59	3	29	38	2	4	34	44	-49
1	25	87	97	2	27	89	-103	3	30	157	172	4	35	-44	-25
1	26	31	36	2	28	36	-32	3	31	-39	-3	4	36	45	-38
1	27	145	160	2	29	57	63	3	32	-40	-17	4	37	79	-92
1	28	48	-49	2	30	64	65	3	33	-40	1	4	38	-45	21
1	29	-34	15	2	31	120	-117	3	34	94	99	4	39	-45	-11
1	30	36	-27	2	32	-38	-17	3	35	-42	-2	4	40	-46	-14
1	31	-36	-20	2	33	74	-84	3	36	53	58	4	41	94	-104

from the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) and, for nickel, the form factor of Viervoll & Øgrim (1949) was used. All observations were weighted equally and non-observed reflections were omitted. The final results are given in Table 1. The calculated and observed structure factors, for which $R=9.87\%$, are listed in Table 2. A Fourier projection of the structure is shown in Fig. 1.

Discussion of the structures of Ce_2Ni_7 and related types

In the following discussion we will use the symbols M and X where M will represent the element which is present in lesser amount and which is of larger atomic size. The M_2X_7 structure of which Ce_2Ni_7 is an example, and the two kinds of MX_3 structure typified by CeNi_3 and PuNi_3 (Cromer & Olsen, 1959), are combinations of MX_2 structures of the MgCu_2 type and MX_5 structures of the CaCu_5 type. All of them may be derived from ordered substitutions of M atoms in the twofold X position of the MX_5 structure followed by appropriate shifts of the layers and small movements of adjacent M atoms in the z direction.

Fig. 2(a) shows several unit cells of the MX_5 structure in projection on a plane normal to the b axis. Fig. 2(b) shows a projection after an M atom has been substituted for an X atom at the $\frac{2}{3}, \frac{1}{3}, 0$ position in every third layer of unit cells in the c direction. This operation has tripled the unit cell and there are now layers of atoms separated by $c/6$. The layers at $z = \frac{1}{6}, \frac{2}{6}, \frac{3}{6}, \frac{4}{6}$ and $\frac{5}{6}$, in alternate unit cells, are now shifted by $x = -\frac{1}{3}$ and $y = \frac{1}{3}$, as indicated by the arrows in Fig. 2(b). This operation doubles the unit cell and we now have a hexagonal cell with the symmetry of space group $P6_3/mmc$ with the same a as MX_5 but with c six times that of the original MX_5 unit cell. The adjacent M atoms are too close to each other and they are now shifted in the z direction to their final positions as shown in the M_2X_7 structure of Fig. 2(c).

The hexagonal CeNi_3 structure is derived as above except that the original substitution of an M atom in the X position is made in alternate unit cells. The rhombohedral PuNi_3 structure is derived in the same manner as the hexagonal CeNi_3 but a different sequence of layer shifts follows the substitution. Fig. 2(d) shows how the layers are shifted to produce the final rhombohedral cell shown in Fig. 2(e).

A substitution of an M atom in every fourth layer would give the composition M_5X_{19} and a hexagonal cell with $c \approx 32 \text{ \AA}$. A substitution in every fifth layer would give the composition MX_4 and a hexagonal cell with $c \approx 40 \text{ \AA}$. Layer shifts to produce rhombohedral cells with these compositions are also possible. M_5X_{19} and MX_4 structures of this nature have not been observed as yet, but it is possible that they exist.

The extreme case of substituting an M atom in every unit cell is shown in Fig. 3(a). The types of shifts indicated by the three sets of arrows lead to the

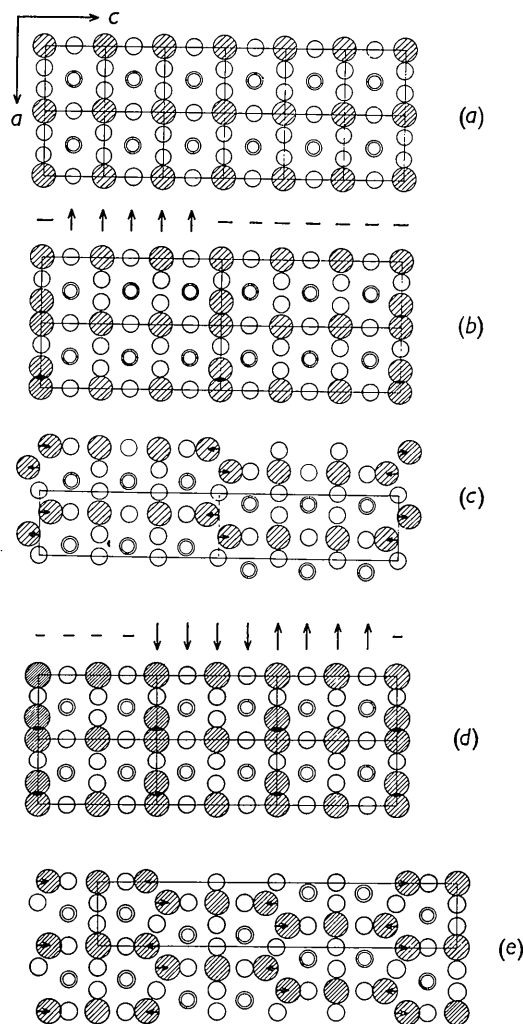


Fig. 2. The larger circles represent the M atoms and the smaller ones the X atoms. An arrow pointing upward indicates a layer shift of $x = -\frac{1}{3}$ and $y = \frac{1}{3}$. An arrow pointing downward indicates a layer shift of $x = \frac{1}{3}$ and $y = -\frac{1}{3}$. A horizontal line indicates that no layer shift occurs. (a) The MX_5 structure in projection on a plane normal to the b axis with M at $0, 0, 0$, $2X$ at $\frac{1}{3}, \frac{2}{3}, 0$ and $\frac{2}{3}, \frac{1}{3}, 0$ and $3X$ at $\frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. (b) An M atom substituted at the $\frac{2}{3}, \frac{1}{3}, 0$ position in every third unit cell with layer shifts indicated that lead to the hexagonal M_2X_7 unit cell. (c) Final M_2X_7 structure with the origin shifted from an M atom to an X atom. (d) An M atom substituted at $\frac{2}{3}, \frac{1}{3}, 0$ in every other unit cell, with layer shifts indicated that lead to a rhombohedral MX_3 unit cell. (e) Final rhombohedral MX_3 unit cell with the origin shifted from an M atom to an X atom.

three kinds of Laves or Friauf phases shown in Fig. 3(b), (c), (d).

The actual Ce_2Ni_7 structure is a slight distortion of the 'ideal' M_2X_7 of Fig. 2(c), because Ni_2 , Ni_3 and Ce_2 are not quite coplanar. The most probable space group is $P6_3/mmc$. If the Ni_4 and/or the Ni_5 atoms are not in position where $y=2x$, the symmetry is reduced to $P\bar{6}2c$. Within the accuracy of our data, the space group is the former and these nickel atoms are in the ideal

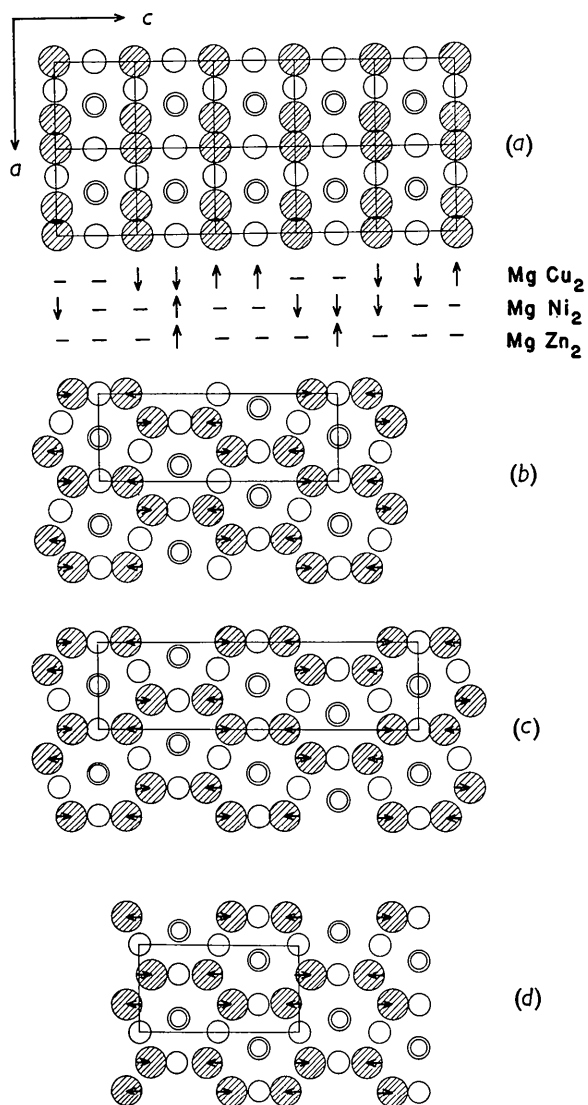


Fig. 3. (a) MX_5 structure with M substituted at $\frac{2}{3}$, $\frac{1}{3}$, 0 in every unit cell. The layer shifts leading to the three different Laves or Friauf phases are indicated. (b) The $MgCu_2$ -type Laves or Friauf phase. The non-primitive hexagonal cell is outlined. This structure is more commonly described as face-centered cubic. (c) The $MgNi_2$ -type Laves or Friauf phase. (d) The $MgZn_2$ -type Laves or Friauf phase.

positions of $P6_3/mmc$ with $x = \frac{5}{8}$. The interatomic distances are shown in Table 3. All are in good agreement with those found in $CeNi_2$, $CeNi_3$ and $CeNi_5$. A drawing of the structure is shown in Fig. 4.

We are indebted to Mr V. O. Struebing for preparation of the cerium-nickel alloy.

Note added in proof:— $PuNi_3$ is isomorphous with $NbBe_3$ whose structure was recently reported by Sands, Zalkin & Krikorian (1959).

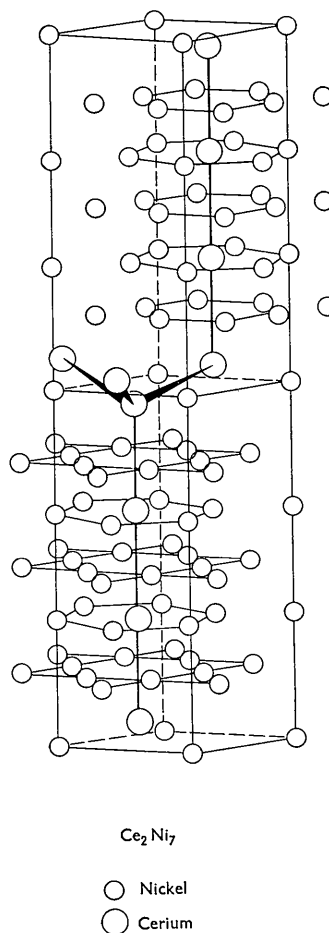


Fig. 4. Drawing of the Ce_2Ni_7 structure.

Table 3. *Interatomic distances in Ce_2Ni_7*

The standard deviation of all distances is about 0.01 Å, primarily because of error in the lattice constants

	Num-ber	Dis-tance	Num-ber	Dis-tance	
Ce_1 to Ce_1	3	3.234 Å	Ni_3 to Ni_2	3	2.875 Å
Ce_2	1	3.542	Ni_4	3	2.500
Ni_1	3	2.969	Ni_5	3	2.458
Ni_5	6	2.833	Ce_2	3	2.882
Ni_5	3	3.178			
Ce_2 to Ce_1	1	3.542	Ni_4 to Ni_2	2	2.491
Ce_2	1	3.693	Ni_3	2	2.500
Ni_2	3	2.881	Ni_4	4	2.490
Ni_3	3	2.882	Ce_2	4	3.100
Ni_4	6	3.100			
Ni_5	6	3.317			
Ni_1 to Ce_1	6	2.969	Ni_5 to Ni_1	1	2.539
Ni_5	6	2.539	Ni_2	1	2.466
			Ni_3	1	2.458
Ni_2 to Ni_3	3	2.875	Ni_5	4	2.490
Ni_4	3	2.491	Ce_1	2	2.833
Ni_5	3	2.466	Ce_1	1	3.178
Ce_2	3	2.881	Ce_2	2	3.317

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The Crystal Structure of ISbCl₈ and IAICl₆

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ISbCl₈ crystallizes in the space group $P4_1$, with four units ISbCl₈ per cell. The coordinates of the Sb and I atoms were found from the [010] Patterson synthesis. Approximate coordinates of the chlorine atoms were obtained by the heavy-atom technique. The coordinates were refined by successive Fourier-syntheses of the [010] projection. The structure consists of ICl₂⁺ and SbCl₆⁻ ions, which are linked to chains by weak covalent bonds.

IAICl₆ crystallizes in the space group $P2_1$ with two units IAICl₆ per cell. The positions of the I atoms were found from Patterson syntheses of the main projections. The positions of the Cl atoms were again determined by the heavy-atom method. This structure consists of chains in which ICl₂⁺ and AlCl₄⁻ ions alternate.

Introduction

Some interhalogen compounds react with metal chlorides to give ionic addition compounds. In the more familiar type of these compounds the interhalogen molecule is used in the formation of a negative ion, e.g. ICl₂⁻, IBrCl⁻, ICl₄⁻, BrF₄⁻, etc. Emeléus and his coworkers have shown that also complex positive ions (BrF₂⁺, IF₄⁺) can be derived from some of the interhalogens. Electrochemical experiments indicate for instance the existence of BrF₂⁺ ions in BrSbF₈ (Woolf & Emeléus, 1949).

We found that ICl₃ reacts quite readily with SbCl₅ and AlCl₃ to give the compounds ISbCl₈ and IAICl₆ respectively (Vonk, 1959). In view of the analogy between the formulae of BrSbF₈ and ISbCl₈ it seemed obvious to assume that ISbCl₈ is built up of ICl₂⁺ and SbCl₆⁻ ions. Some electrochemical experiments, in which POCl₃ and liquid SO₂ were used as solvents, were undertaken to verify this assumption. These experiments however failed because ISbCl₈ decomposes in both solvents. It was therefore decided to determine the structures of both ISbCl₈ and IAICl₆ by X-ray diffraction.

ISbCl₈

This compound is obtained as red needle-like crystals when a hot solution of ICl₃ in SbCl₅ is allowed to cool to room temperature. It is also formed when Cl₂ gas is passed through a solution of ICl in SbCl₅.

ISbCl₈ is rapidly attacked by moist air, while on

heating it decomposes at about 60 °C. into SbCl₅, ICl and Cl₂. During the X-ray exposures the crystals were kept in thin-walled pyrex tubes.

The photographs showed tetragonal symmetry.

Unit cell:

$$a=b=6.98 \pm 0.03, \quad c=24.2 \pm 0.1 \text{ \AA}.$$

Reflections $00l$ absent for $l \neq 4n$. Space group $P4_1$. Density, calculated from the unit-cell volume, assuming 4 ISbCl₈ units per cell: 3.00 g.cm.⁻³. Observed density 3.0(±0.2) g.cm.⁻³. Crystal habit: Rapidly grown crystals are needle-like along [001] and show the forms {100}, {001} and {101}. Slowly grown crystals may also show the forms {102}, {103} and {104}.

Intensities

The intensities of 68 reflections $hk0$ and 161 reflections $h0l$ were obtained from integrated and non-integrated Weissenberg photographs taken with Zr-filtered Mo-radiation.

The dimensions of the crystal used for the determination of the intensities $h0l$ were: 0.06 (rotation axis) × 0.06 × 0.16 mm. Because of the relatively large dimensions of the cross section perpendicular to the rotation axis and the relatively large linear absorption coefficient $\mu=70 \text{ cm.}^{-1}$, a correction for absorption was applied. For the reflections $hk0$ the absorption correction was neglected, since these reflections were obtained from a crystal with a cross section of $0.04 \times 0.04 \text{ mm.}^2$ perpendicular to the rotation axis.