forces, and four of these partially metallic bonds have more energy than eight normal van der Waals bonds with a distance of the order of 4 A.

The fact that α-selenium consists of finite ring molecules rather than infinite chains makes it quite obvious why such profound differences exist in the physical properties of α-selenium and metallic selenium. On the other hand, the ring configuration is not a very satisfactory one for selenium as shown by the readiness with which it transforms to the metallic structure on heating.

The writer believes that the shortest packing distances observed in α-selenium are a manifestation of this unstable state of things. They indicate that the atoms involved are being appreciably polarized by atoms in the neighboring molecules. When the ring molecules break open to form chains it is probably these atoms which initiate the process. Also it is clear why the stability of metallic selenium is so high relative to α-selenium. In α-selenium there are at the most only three or four of these shorter intermolecular bonds per eight-atom unit, while in metallic selenium there are 32 intermolecular bonds for every eight atoms.

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The Crystal Structures of NiO.3BaO, NiO.BaO, $BaNiO_3$ and Intermediate Phases with Composition near $Ba_2Ni_2O_5$; with a Note on NiO

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The crystal structures of NiO.3BaO, NiO.BaO and $BaNiO_3$ have been determined from X-ray diffraction data, and data are given for phases with composition near that represented by $Ba_2Ni_2O_5$. In each of these structures nickel behaves in a novel fashion. A coplanar triangular arrangement of oxygen around nickel is found in NiO.3BaO. In $BaNiO_3$ nickel has a valence of four and the structure is a close-packed hexagonal stacking of planar arrangements found in perovskite 111 planes. The compound NiO.BaO has a magnetic moment corresponding to two unpaired electrons, whereas the deduced coplanar square arrangement of oxygen around nickel suggests that there should be no unpaired electrons. Compounds with composition near $Ba_2Ni_2O_5$ contain an amount of oxygen which is a continuous function of temperature and possibly contain mixtures of bi- and tetravalent nickel.

The problem of NiO having octahedral co-ordination of oxygen is considered.

Introduction

Current papers (Lander, 1951; Lander & Wooten, 1951) discuss the preparation and properties of barium–nickel oxides. Compounds containing nickel in a valence state higher than two are particularly interesting because relatively little is known about them. A search of the crystallographic literature revealed no studies of such compounds, though there are reports in the chemical literature of mixed oxides in which nickel probably has a valence greater than two. Concerning barium–nickel oxides: Goralevich (1930*a*, *b*, *c*) fused NiO with $Ba(NO_3)_2$ and from the mixture separated compounds to which he assigned the formulae $BaNiO_3$ and $BaO_2.NiO_3$; the compound $BaNi_2O_5$ described by Dufau (1896, 1897) was not found in the present work, perhaps because the conditions of his experiments were not exactly reproduced; Thurber (1937) observed that NiO and $BaCO_3$ in O_2 react to form several compounds which he did not isolate and identify.

The investigation of the system Ba–Ni–O as a function of temperature and oxygen pressure was facilitated by systematic X-ray diffraction analyses of the products. By this means new phases were quickly recognized and the efficacy of methods of purification was checked. Moreover, the results of the structure analyses reported herein may be added to other evidence leading to the identification of the phases.

Structure determinations of NiO.3BaO and $BaNiO_3$ have been made entirely from the powder patterns. Single crystals were not obtained. Single crystals of NiO.BaO and a phase with composition near $Ba_2Ni_2O_5$ were grown, and rotation photographs of them were taken. A fifth distinct phase was observed but not obtained pure. Nickel-filtered Cu $K\alpha$ radiation was used for all powder and rotation photographs but one. Back-reflection Laue patterns were obtained from NiO.BaO.

The structure of NiO.3BaO

The compound with the chemically determined composition NiO.3BaO has properties that one might expect of a solid solution of NiO in BaO. It is grey-green and unstable in moist air. The powder-pattern data were indexed on a hexagonal cell (rhombohedral system) with $a_0 = 7{\cdot}85$ and $c_0 = 16{\cdot}50$ A. This corresponds to a rhombohedral cell with $a_0 = 7{\cdot}14$ A. and $\alpha = 66{\cdot}8^\circ$ having a volume of 293 A.^{3}. The sum of the volumes of six BaO molecules in cubic BaO and two NiO molecules in cubic NiO is 294 A.^{3}. Thus there should be two NiO.3BaO molecules per unit rhombohedral cell and six per unit hexagonal cell.

The more intense lines of the powder pattern, indexed hexagonally, fit the supplementary conditions: $(h.h.\overline{2h}.l)$ with $l = 3n$; $(h\bar{h}0l)$ with $2h + l = 3n$ and $l = 2n$; $(hkil)$ with $h - k + l = 3n$ and $l = 2n$. These are characteristic of the space group D^6_{3d}–$R\bar{3}c$. The most general sixfold rhombohedral positions of the space group are:

$$x, \tfrac{1}{2}-x, \tfrac{1}{4};\quad \tfrac{1}{2}-x, \tfrac{1}{4}, x;\quad \tfrac{1}{4}, x, \tfrac{1}{2}-x;$$
$$\bar{x}, \tfrac{1}{2}+x, \tfrac{3}{4};\quad \tfrac{1}{2}+x, \tfrac{3}{4}, \bar{x};\quad \tfrac{3}{4}, \bar{x}, \tfrac{1}{2}+x.$$

There is little ambiguity in using the estimated intensities of the powder pattern to determine the co-ordinates of the barium ions because relatively few reflections coincide and because the intensities are overwhelmingly determined by these ions (the ratio of the structure factors f_{Ba}: f_{Ni}: f_{O} is approximately $2{\cdot}2:1:0{\cdot}2$). Weak and absent features in the first and second orders yield $x = \frac{2}{3}$, and with the co-ordinates thus determined intensities are calculated which are a good approximation to the observed intensities.

At this point it is important to examine the structure so far determined. Since neither nickel nor oxygen can be located with a high degree of accuracy by intensity analysis, the most probable arrangement must be determined from the point of view of space, symmetry and the properties of the ions. The arrangement of barium ions is more clearly seen in the hexagonal cell (see Fig. 1). They have been placed in octahedral arrays centering on the six positions

$$(0, 0, 0;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{3};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{2}{3}) + (0, 0, 0;\ 0, 0, \tfrac{1}{2}).$$

From a barium ion center to the center of the octahedron the distance is 2·78 A. Obviously an oxygen ion must fill each octahedron. Thus six of the twenty-four oxygen ions of the hexagonal cell have been located.

The barium octahedra share corners and symmetrically surround the six cavities with centers at the positions

$$(0, 0, 0;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{3};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{2}{3}) + (0, 0, \tfrac{1}{4};\ 0, 0, \tfrac{3}{4}).$$

But there are six nickel ions and eighteen oxygen ions left to fill these volumes, or one nickel and three oxygen ions per volume. The most likely location for the nickel ion is at the center. The oxygen ions are now placed where there is room for them which, in the rhombohedral cell, turns out to be at

$$0, \tfrac{1}{2}, \tfrac{1}{4};\ \tfrac{1}{2}, \tfrac{1}{4}, 0;\ \tfrac{1}{4}, 0, \tfrac{1}{2};\ 0, \tfrac{1}{2}, \tfrac{3}{4};\ \tfrac{1}{2}, \tfrac{3}{4}, 0;\ \tfrac{3}{4}, 0, \tfrac{1}{2}.$$

These may be obtained from the general sixfold positions of the space group given above by setting $x = 0$, and they place oxygen ions in coplanar triangular array around nickel ions.

Details of the calculation of intensities are given in Table 1. To a sufficient approximation the relative intensity of a reflection I_{hkl} is given by:

$$\begin{aligned}\{f_{\mathrm{Ba}} \times 2\ [&\cos \tfrac{1}{6}\pi(4h+2k+9l) + \cos \tfrac{1}{6}\pi(2h+9k+4l)\\ &+ \cos \tfrac{1}{6}\pi(9h+4k+2l)] + f_{\mathrm{Ni}} \times 2 \cos \tfrac{1}{2}\pi\ (h+k+l)\\ &+ f_{\mathrm{O}} \times [1 + \cos \pi(h+k+l) + 2\{\cos \pi(h+\tfrac{1}{2}k)\\ &+ \cos \pi(k+\tfrac{1}{2}l) + \cos \pi(\tfrac{1}{2}h+1)\}]\}^2.\end{aligned}$$

Polarization and temperature factors have been omitted. Atomic structure factors have been taken from the *International Tables*... (1935). The columns of Table 1 list the rhombohedral indices *hkl*, observed values of interplanar spacings $d_{\mathrm{obs.}}$, calculated values $d_{\mathrm{calc.}}$, the value $I_{hkl}(\times 10^{-3})$ multiplied by the plane multiplicity m, and the estimated intensity $I_{\mathrm{obs.}}$ relative to a maximum equal to 10.

Since the agreement between calculated and observed intensities is very good through the hundred and twenty reflections (and more which have not been tabulated), further adjustment of the parameters has not been attempted.

The structure may be arrived at by simple translations of points of the sodium chloride structure and the co-ordinates of the sodium chloride structure are

Table 1. *Data for* NiO.3BaO

hkl	$d_{\text{obs.}}$	$d_{\text{calc.}}$	mI_{hkl}	$I_{\text{obs.}}$
100	—	6·27	15	—
110	—	5·24	3	—
$\bar{1}10$	3·88	3·92	23	2
211	3·50	3·53	0	$\frac{1}{8}$
210	3·18	3·19	135	10
200	3·12	3·13	150	8
222	2·75	2·75	232	8
220	2·62	2·62	310	10
$\bar{2}10$	2·54	2·54	252	8
$\bar{2}11$	2·25	2·26	132	5
321		2·26	44	
320	2·02	2·02	106	4
332	—	1·972	14	—
$\bar{2}20$	1·950	1·955	38	1
221	1·872	1·870	440	8
$3\bar{1}1$	1·844	1·845	61	1
$\bar{3}10$	1·830	1·833	34	$\frac{1}{2}$
422	1·764	1·763	309	2
330	1·746	1·746	80	$1\frac{1}{2}$
411		1·746	80	
421	1·755	1·735	95	1
$32\bar{1}$	1·711	1·711	36	$\frac{1}{4}$
$\bar{2}22$	1·665	1·661	7	$1\frac{1}{2}$
432		1·66	99	
410	1·635	1·635	202	3
433	—	1·602	3	—
420	1·596	1·596	27	$\frac{1}{4}$
400	1·568	1·568	23	$\frac{1}{4}$
$3\bar{2}1$	1·528	1·528	160	2
442	1·488	1·484	168	2
430	1·472	1·471	190	3
$4\bar{1}1$	1·457	1·456	216	2
$3\bar{2}2$	1·428	1·429	49	1
410		1·429	25	
$42\bar{1}$	1·409	1·408	24	$\frac{1}{4}$
521	1·395	1·392	19	$\frac{1}{4}$
444	1·381	1·375	146	$1\frac{1}{2}$
$\bar{4}11$	1·341	1·338	162	2
531		1·336	24	
440	—	1·308	17	—
$\bar{3}30$	—	1·305	20	—
$43\bar{1}$	—	1·302	2	—
510	—	1·302	1	—
542	1·299	1·295	65	$\frac{1}{2}$
543	—	1·294	16	—
$33\bar{2}$	1·290	1·288	300	2
$\bar{3}31$	1·277	1·278	160	$\frac{3}{4}$
$4\bar{2}1$	1·268	1·268	250	$1\frac{1}{2}$
$\bar{4}20$		1·265	20	
530	1·242	1·241	86	1
541		1·240	22	
$4\bar{2}2$	—	1·223	3	—
$\bar{4}21$	—	1·213	33	—
$\bar{3}32$	—	1·205	25	—
$5\bar{1}1$	1·194	1·192	140	$\frac{1}{2}$
622	—	1·182	8	—
$52\bar{1}$	—	1·179	25	—
552	1·175	1·175	65	$\frac{3}{4}$
633		1·175	65	
$\bar{5}10$	—	1·166	15	—
554	—	1·161	2	—
540	1·150	1·151	18	$\frac{1}{4}$
621		1·151	18	
$43\bar{2}$	—	1·144	39	—
611	1·134	1·133	256	1
631		1·132	2	
$63\bar{1}$	1·127	1·130	100	$\frac{1}{2}$
643		1·130	32	
$\bar{4}22$		1·129	14	
642	—	1·125	20	—
432	1·117	1·119	115	$\frac{1}{4}$
644	1·112	1·113	120	$\frac{1}{4}$
$\bar{4}30$	—	1·110	19	—
620	1·086	1·088	7	1
$\bar{4}31$		1·085	325	
610		1·082	18	
$5\bar{2}1$	—	1·077	42	—
$4\bar{3}2$	1·064	1·065	36	1
$\bar{5}20$		1·065	50	
630		1·063	115	
654		1·060	72	
$5\bar{2}2$	—	1·056	17	—
$54\bar{1}$	1·054	1·049	14	1
550		1·049	210	

All other features (36) in this range have zero calculated intensity and were absent.

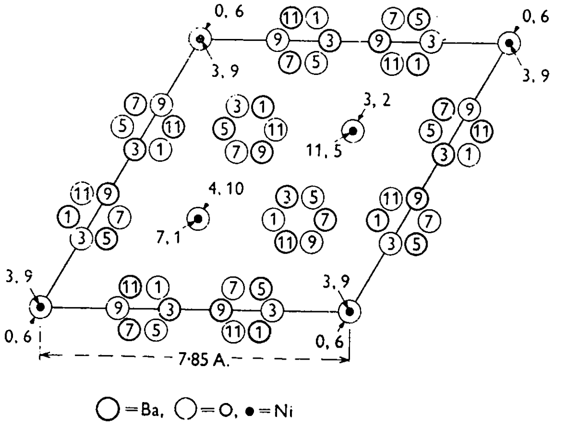

Fig. 1. The unit hexagonal cell of NiO.3BaO projected on $(a\ b)$. Numbers indicate the c_0 co-ordinates in twelfths. $a_0=7{\cdot}85$, $c_0=16{\cdot}50$ A.

contained in the co-ordinates of the space group. Fig. 1 is a projection of the unit hexagonal cell on $(a\ b)$. Perhaps the most unusual feature of the structure is the coplanar triangular co-ordination of oxygen ions with nickel. The oxygen co-ordinates were arbitrarily chosen to make the computations simple. They result in the value 1·96 A. for Ni–O distances, and this makes the distance between an oxygen of the plane triangle and the nearest barium ion equal to 2·82 A. Although these distances cannot be in error by more than a few per cent, it is likely that the Ni–O distance should be increased and the Ba–O distance decreased.

The structure obeys the electrostatic valence rule. Each barium ion is surrounded by seven nearest oxygen ions, each nickel ion by three oxygen ions and each oxygen ion by five barium ions and one nickel ion. The valence of oxygen is calculated to be 2·10.

Summarizing the structure:

The space group is D_{3d}^{6}–$R\bar{3}c$.

Rhombohedral cell: $a_0=7{\cdot}14$ A., $\alpha=66{\cdot}8°$.

2 Ni at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}$.

2 O at $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

6 Ba at $\frac{2}{3}, \frac{5}{6}, \frac{1}{4}; \frac{5}{6}, \frac{1}{4}, \frac{2}{3}; \frac{1}{4}, \frac{2}{3}, \frac{5}{6}; \overline{\tfrac{2}{3}}, \overline{\tfrac{5}{6}}, \overline{\tfrac{1}{4}}; \overline{\tfrac{5}{6}}, \overline{\tfrac{1}{4}}, \overline{\tfrac{2}{3}}; \overline{\tfrac{1}{4}}, \overline{\tfrac{2}{3}}, \overline{\tfrac{5}{6}}$.

6 O at $x, \frac{1}{2}-x, \frac{1}{4}; \frac{1}{2}-x, \frac{1}{4}, x; \frac{1}{4}, x, \frac{1}{2}-x; x, \frac{1}{2}+x, \frac{3}{4}; \frac{1}{2}+x, \frac{3}{4}, \bar{x}; \frac{3}{4}, \bar{x}, \frac{1}{2}+x$. x very near 0.

Hexagonal cell $a_0 = 7{\cdot}85$ A., $c_0 = 16{\cdot}50$ A.

Add $(0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{3}; \frac{2}{3}, \frac{1}{3}, \frac{2}{3}) = (A)$ to obtain:

6 Ni at $(0, 0, \frac{1}{4}; 0, 0, \frac{3}{4}) + (A)$,

6 O at $(0, 0, 0; 0, 0, \frac{1}{2}) + (A)$.

18 Ba at $(\frac{5}{12}, 0, \frac{1}{4}; 0, \frac{5}{12}, \frac{1}{4}; \frac{\bar{5}}{12}, \frac{\bar{5}}{12}, \frac{1}{4}; \frac{\bar{5}}{12}, 0, \frac{\bar{1}}{4}; 0, \frac{\bar{5}}{12}, \frac{\bar{1}}{4}; \frac{5}{12}, \frac{5}{12}, \frac{1}{4}) + (A)$.

18 O at $(x, 0, \frac{1}{4}; 0, x, \frac{1}{4}; \bar{x}, \bar{x}, \frac{1}{4}; \bar{x}, 0, \frac{3}{4}; 0, x, \frac{3}{4}; x, x, \frac{3}{4}) + (A)$. x very near $\frac{9}{12}$.

The structure of NiO.BaO

NiO.BaO is a black substance, stable in air and insoluble in water and alkali. Single crystals are easily grown at about 1000° C. in N_2 in a flux of $BaCl_2$, or $2BaCO_3.BaO$. The crystals obtained using either flux were rectangular plates with truncated ends and edges. The dihedral angles were found to be very nearly 120°.

Rotation photographs, back-reflection Laue patterns and powder patterns were taken. The rotation photographs led to an orthorhombic cell. The powder pattern, calibrated with NaCl, gave the cell constants

$$a_0 = 5{\cdot}73, \quad b_0 = 9{\cdot}20 \quad \text{and} \quad c_0 = 4{\cdot}73 \text{ A.}$$

The volume is 249 A.^{3}. The volume of four molecules of BaO in cubic BaO plus four molecules of NiO in cubic NiO is 245 A.^{3}. Therefore there are four NiO.BaO molecules per unit cell.

The Laue pattern obtained with radiation parallel to the c_0 axis was found to have sixfold rotational symmetry. Moreover the value of b_0/a_0 is 1·605 (the orthohexagonal value is 1·732). These observations suggest a pseudo-hexagonal structure and the number of barium ions per unit cell indicates a close-packed rather than a rhombohedral arrangement of barium ions. Extinctions appeared to be characteristic of D_2^5 or D_{2h}^{17}, but many space groups are possible.

Intensities calculated with barium ions at $0, \frac{1}{3}, \frac{1}{4}; \frac{1}{2}, \frac{5}{6}, \frac{1}{4}; 0, \frac{\bar{1}}{3}, \frac{\bar{1}}{4}; \frac{\bar{1}}{2}, \frac{\bar{5}}{6}, \frac{\bar{1}}{4}$ agree well with the observed intensities of the powder pattern. Accepting these, likely positions for the nickel ions are $0, 0, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ or $0, 0, \frac{1}{4}; 0, 0, \frac{3}{4}; \frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4}$. Improved agreement is obtained with the first but not the second. Orthorhombic space groups having the barium coordinates and the first set of nickel co-ordinates are D_2^5, D_{2h}^{14} and D_{2h}^{17}.

Oxygen ions necessarily have a marginal effect on the intensities and therefore they are more accurately located by space, symmetry and potential considerations. Probable co-ordinates for the eight oxygen ions are $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + (x, y, \frac{1}{4}; \bar{x}, y, \frac{1}{4}; x, \bar{y}, \frac{3}{4}; \bar{x}, \bar{y}, \frac{3}{4})$, with x near $\frac{1}{4}$ and y near $\frac{1}{12}$. These parameters place oxygen ions at approximately the expected distance from nearest nickel and barium ions. A calculation of intensities using the co-ordinates given above gives excellent agreement with the observed intensities except for k large and $h + k = 2n$. This discrepancy can be adjusted by placing the barium ions at $0, \frac{1}{3} + \frac{1}{96}, \frac{1}{4}; \frac{1}{2}, \frac{5}{6} + \frac{1}{96}, \frac{1}{4}; 0, \overline{\frac{1}{3} + \frac{1}{96}}, \frac{1}{4}; \frac{1}{2}, \overline{\frac{5}{6} + \frac{1}{96}}, \frac{\bar{1}}{4}$. Relative values of I_{hkl} are given by

$$\{f_{Ba} \times 4 \cos \tfrac{1}{6}\pi[3h + (7 + \tfrac{1}{8})\, k + 3l] \cos \tfrac{1}{2}\pi(h + k)$$
$$+ f_{Ni} \times 4 \cos \tfrac{1}{2}\pi(h + k + l) \cos \tfrac{1}{2}\pi(h + k) \cos \tfrac{1}{2}\pi l$$
$$+ f_O \times 8 \cos \tfrac{1}{2}\pi h \cos \tfrac{1}{2}\pi k \cos \tfrac{1}{6}\pi(6h + 4k + 3l)\}^2,$$

in which polarization factors, etc., have been omitted, as in the calculation and tabulation of data for NiO.3BaO above. In regions where two or more reflections overlap, the estimated intensity from the powder pattern has been distributed among the reflections in a ratio obtained from the rotation photograph. In general relative intensities estimated from the powder pattern were considered more reliable than those from the single-crystal photographs.

Table 2. *Data for* NiO.BaO

hkl	$d_{obs.}$	$d_{calc.}$	mI_{hkl}	$I_{obs.}$
020	4·58	4·60	2	$\frac{1}{4}$
111	3·39	3·39	230	10
021	3·28	3·30	58	2
200	2·85	2·86	101	3
130	2·70	2·71	270	10
220	2·41	2·43	3	$\frac{1}{8}$
002	2·37	2·37	48	1
131	2·35	2·35	15	$\frac{1}{4}$
040	2·295	2·30	9	$\frac{1}{4}$
221	2·164	2·162	260	8
112	2·132	2·128	207	5
022	2·110	2·105	60	$1\frac{1}{2}$
041	2·065	2·070	102	3
310	1·868	1·871	2	$\frac{1}{8}$
202	1·831	1·835	3	$\frac{1}{4}$
240	—	1·795	2	$\frac{1}{8}$
132	1·783	1·781	60	1
150	—	1·755	4	—
311	1·743	1·740	154	2
222	1·697	1·696	220	3
241	1·674	1·678	50	$\frac{1}{2}$
042	1·652	1·651	140	2
151	1·640	1·643	155	3
330	1·622	1·622	194	3
060	1·531	1·536	60	$\frac{3}{4}$
113	1·506	1·501	130	$1\frac{1}{2}$
023	1·495	1·492	42	$\frac{1}{2}$
312	1·471	1·470	196	2
061	1·455	1·457	15	$\frac{1}{8}$
400	1·431	1·433	115	3
242		1·430	184	
152	1·408	1·408	72	$\frac{1}{2}$
260	1·348	1·353	180	2
332	1·340	1·338	45	$\frac{1}{2}$
421	1·315	1·314	80	1
043	1·304	1·302	54	$\frac{1}{2}$
261	1·298	1·300	23	$\frac{1}{8}$
062	—	1·287	8	—
170	—	1·281	5	—
351	1·275	1·277	137	2
171	1·232	1·236	56	$\frac{1}{2}$
402	1·224	1·226	35	$\frac{1}{4}$
440	—	1·216	7	—
313	1·206	1·206	100	$\frac{3}{4}$
422	1·186	1·185	90	$1\frac{1}{2}$
004		1·183	89	
441	1·175	1·178	95	$\frac{3}{4}$
262		1·176	65	$\frac{1}{2}$
153		1·173	123	$\frac{3}{4}$
352	1·156	1·158	55	$\frac{1}{4}$
080	—	1·150	3	—

All other features (69) in this range have zero calculated intensity and were absent.

Calculated intensities are in good agreement with the estimated intensities, so further adjustment of the parameters has not been attempted.

The structure assigns four oxygen ions to a planar and very nearly square arrangement around nickel. The squares share edges in both the a_0 and the c_0 directions. In the c_0 direction strings of squares each containing a nickel ion alternate with strings of empty squares. In the a_0 direction the O–O distance is 2·86 A., and the other O–O distance is 2·82 A. Ni–O distances are 2·01 A. and Ni–Ni distances are 2·365 A. Barium is surrounded by eight oxygen ions with Ba–O distances equal to 2·84 and 2·80 A. Ba–Ba distances projecting along b_0 are 3·71 A. and others are 4·10 A. The angle of the pseudo-hexagonal cell is 58·1°.

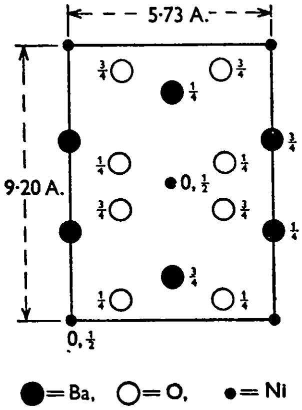

Fig. 2. The unit orthorhombic cell of $NiO.BaO$ projected on $(a\ b)$. Numbers indicate the fractional c_0 co-ordinates. $a_0=5{\cdot}73$, $b_0=9{\cdot}20$, $c_0=4{\cdot}73$ A.

A projection of the structure in the c_0 direction is given in Fig. 2. Barium and nickel positions are believed to be known with sufficient precision to rule out the possibility of tetrahedral co-ordination of oxygen, though the co-ordinates assigned to oxygen may be in error by several percent. The interatomic distances may be compared with those observed in a perovskite structure with a cation similar to nickel, for example, $BaTiO_3$. The structures are similar in the arrangements of ions in $(a\ b)$ planes, but the stacking of these planes is close-packed hexagonal rather than rhombohedral. All the interatomic distances are close to those expected except that of Ni–Ni. This distance is 2·36 A. The valence computed for oxygen by applying the electrostatic valence rule is 2·0.

Summary of the structure of $NiO.BaO$:

Orthorhombic cell with $a_0=5{\cdot}73$, $b_0=9{\cdot}20$, $c_0=4{\cdot}73$ A.

Space group D_{2h}^{17}–$Cmcm$.

4 Ni at $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+(0, 0, 0;\ 0, 0, \frac{1}{2})$.

8 O at $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+(x, y, \frac{1}{4};\ \bar{x}, y, \frac{1}{4};\ x, \bar{y}, \frac{3}{4};\ \bar{x}, \bar{y}, \frac{3}{4})$, with x very near $\frac{1}{4}$ and y very near $\frac{1}{12}$.

4 Ba at $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+(0, y, \frac{1}{4};\ 0, \bar{y}, \frac{1}{4})$, with y equal to $\frac{11}{32}$.

The structure of $BaNiO_3$

$BaNiO_3$ is obtained as a black powder, insoluble in alkali and water but soluble in acid, by heating an intimate mixture of BaO_2 and NiO in O_2. Reaction is appreciable at 450 and above 730° C., in O_2 at about 740 mm. of Hg, the compound decomposes. Single crystals were not obtained, but it seems likely that they can be grown in a properly controlled $Ba(OH)_2.xH_2O$ flux or by long exposure of a crystal of $NiO.BaO$ to oxygen.

Superficial examination of the powder pattern obtained leads to a cubic structure with a_0 equal to 4·832 A. However, among the integers $h^2+k^2+l^2$ for the reflections one finds all those which cannot occur in the cubic system (e.g. 7, 15, 23). When all are present, enlarging the unit cell does not escape the difficulty.

A hexagonal cell with $a_0=5{\cdot}580$ and $c_0=4{\cdot}832$ A. $(d=5{\cdot}58/\sqrt{[h^2+k^2+hk+l^2]})$ satisfies the observed integer sequence. The volume of the cell is 130·4 A.^{3}. Therefore there is room for two molecules of $BaNiO_3$ per unit cell (compare with four $NiO.BaO$ having the volume 249 A.^{3}).

The pseudo-cubic character of the hexagonal cell means that coincidence of several types of reflections is the rule rather than the exception. A characteristic space group is not immediately obvious, since few extinctions show up in the powder pattern.

Barium ions at $\frac{2}{3}, \frac{1}{3}, \frac{3}{4};\ \bar{\frac{2}{3}}, \bar{\frac{1}{3}}, \bar{\frac{3}{4}}$ and nickel ions at $0, 0, 0;\ 0, 0, \frac{1}{2}$ were found to give sets of intensities in good agreement with those observed. Accepting these co-ordinates and assuming six oxygen ions of one kind (in particular assuming the absence of peroxide ions) limits the possible hexagonal space groups to C_{3i}^1, D_3^2, D_{3d}^2, D_{3d}^3, C_6^6, C_{6h}^2, D_{3h}^4, C_{6v}^4, D_6^6, D_{6h}^4. The six co-ordinates with the highest symmetry are $x, 2x, \frac{1}{4};\ \overline{2x}, \bar{x}, \frac{1}{4};\ x, \bar{x}, \frac{1}{4};\ \bar{x}, \overline{2x}, \frac{3}{4};\ 2x, x, \frac{3}{4};\ \bar{x}, x, \frac{3}{4}$. The value $x=\frac{1}{6}$ places oxygen ions on corners of octahedra with nickel ions in the centers, the Ni–O distance is 2·01 A., and barium ions are surrounded by twelve oxygen ions with six Ba–O distances equal to 2·90 A. and six equal to 2·79 A. The valence of oxygen calculated by the electrostatic valence rule is 2·0. A projection on $(a\ b)$ is given in Fig. 3. The structure type has been discussed by Burbank & Evans (1948).

Details of the calculation of intensities for the above structure are to be found in Table 3. The relative intensity of a reflection I_{hkl} is

$$\{f_{\mathrm{Ba}}\times 2\cos\tfrac{1}{6}\pi(-4h+4k+3l)+f_{\mathrm{Ni}}\times(1+\cos\pi l) +f_{\mathrm{O}}\times 2[\cos\tfrac{1}{6}\pi(2h+4k+3l)+\cos\tfrac{1}{6}\pi(2h+2k+3l) +\cos\tfrac{1}{6}\pi(8h-2k+3l)]\}^2.$$

The agreement between calculated and estimated intensities is good. One can be confident that the co-ordinates assigned to nickel are not grossly in error (10% or more), and the choice of positions with high symmetry is demanded by the high symmetry of the pattern. If the nickel ions have been exactly located,

Table 3. *Data for* $BaNiO_3$

hkl	$d_{obs.}$	$d_{calc.}$	mI_{hkl}	Σ	$I_{est.}$
001 100	—	4·832	0 0·2	0·2	—
101	3·43	3·42	61	61	5
110	2·79	2·79	92	92	6
111 200 002	2·42	2·42	0 2·2 12·6	14·8	2
201 102	2·167	2·162	112 72	184	10
112 210	1·826	1·827	14·6 0	14·6	2
211 202	1·709	1·709	132 88	220	8
310 003	1·607	1·610	64 0	64	3
301 103	1·530	1·528	0 41·5	41·5	2
302 212	1·457	1·457	15 108	123	4
220 113	1·393	1·395	92 0	92	4
310 221 302 203	1·340	1·340	0 0 25 67	92	4
311	1·291	1·291	70	70	3
400 222 213 004	1·208	1·209	1 23 65 72	161	6
401 312 104	1·171	1·172	43 79 0	122	4
303	—	1·139	0	—	—
114 320	1·108	1·108	85 0·5	85	2
321 402 204	1·079	1·081	58 50 15	123	3
410 223	1·053	1·054	85 0	85	2
411 313	1·030	1·030	0 53	53	1
322 214	1·007	1·008	66 66	64	$\frac{3}{4}$
500 412 403 304 005	0·9951	0·967	0 19 18 76 0	113	3
501 105	0·947	0·948	25 25	50	1
330	0·931	0·930	35	35	$\frac{1}{2}$
420 331 323 224 115	0·912	0·913	0 0 49 132 0	181	3
421 314 205 502	0·8965	0·8975	34 1 17 27	79	2
413	—	0·8825	0	—	—
510 332	0·8672	0·8680	0·5 10·5	11	$\frac{1}{2}$
511 422 404 215	0·8538	0·8544	76 43 1 24	144	3
512 324	0·8158	0·8170	53 1	54	1
600 333	0·8044	0·8055	43 0	43	$\frac{1}{2}$
430 601 423 414 225 106 006	0·7935	0·7943	3 0 31 117 0 26 3	180	4

then there is little space left and the oxygen coordinates given are correct to about 1 %.

The problem of primary importance is whether or not the compound is a mixed oxide–peroxide (e.g. $BaO_2.NiO$). But placing Ba at $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \frac{2}{3}, \frac{1}{3}, \frac{1}{4}$ leaves no hexagonal space group with a sufficiently general set of twofold positions to accommodate two oxygen ions and two peroxide ions. Thus, although intensity analysis places nickel ions with only fair accuracy and oxygen ions with hardly any at all, nevertheless the very high symmetry reflected by the pattern and the location of the cations make it highly unlikely that the material is a mixed oxide–peroxide. Chemical tests for peroxide in the material were also negative.

The structure assigned above belongs to the space group C_{6v}^4–*C6mc*. It is closely related to the perovskite structure. The (111) layers of that structure are reproduced identically but they are stacked with barium ions falling in a hexagonal close-packed arrangement. Oxygen ions form octahedra each containing a nickel ion. The principal difference between the two structures is found in the arrangement of nickel ions. In a perovskite structure nickel ions would be separated by an oxygen ion, the Ni–Ni distance would be about 4·00 A. and oxygen octahedra would share corners. In the assigned structure the oxygen octahedra share faces and the Ni–Ni distance is 2·42 A. A projection of the unit cell on (*a b*) is given in Fig. 3.

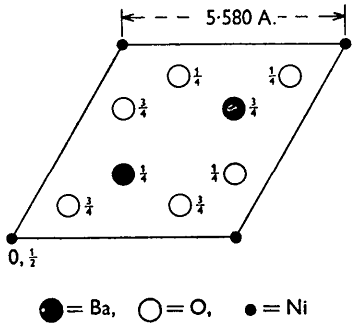

Fig. 3. The unit hexagonal cell of $BaNiO_3$ projected on (*a b*). $a_0 = 5{\cdot}580$, $c_0 = 4{\cdot}832$ A.

Summary of the structure of $BaNiO_3$:

Hexagonal cell with $a_0 = 5{\cdot}580$ and $c_0 = 4{\cdot}832$ A.

Space group C_{6v}^4–*C6mc*.

2 Ba at $\frac{2}{3}, \frac{1}{3}, \frac{3}{4}; \frac{1}{3}, \frac{2}{3}, \frac{1}{4}$.

2 Ni at 0, 0, 0; 0, 0, $\frac{1}{2}$.

6 O at $\frac{1}{6}, \frac{1}{3}, \frac{1}{4}; \frac{1}{6}, \frac{5}{6}, \frac{1}{4}; \frac{2}{3}, \frac{5}{6}, \frac{1}{4}; \frac{5}{6}, \frac{1}{6}, \frac{3}{4}; \frac{1}{3}, \frac{1}{6}, \frac{3}{4}; \frac{5}{6}, \frac{2}{3}, \frac{3}{4}$.

Intermediate phases with composition near $Ba_2Ni_2O_5$

Fusion at about 1000° C. in $BaCl_2$, $Ba(OH)_2$ or $BaO.2BaCO_3$ of an equimolar mixture of BaO_2 and NiO yields black acicular crystals with the approximate composition $Ba_2Ni_2O_5$. Rotation photographs of such crystals are simply interpreted to a first approximation. They are nearly hexagonal with a_0 about 5·70 and c_0 about 4·42 A. Indexed hexagonally, the strong reflections are 110, 300, 220, 101, 201, 112, 211, etc. Therefore barium ions are near $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}; \frac{1}{3}, \frac{2}{3}, \frac{3}{4}$, and the gross structure resembles those of NiO.BaO and $BaNiO_3$, given above.

The complexity of fine structure of the patterns obtained from one crystal has discouraged a complete analysis. All the reflections are either doublets or triplets. To a better approximation the cell is orthorhombic with

$$a_0 = n_1 \times 5{\cdot}75,\ b_0 = n_2 \times 9{\cdot}71,\ \text{and}\ c_0 = n_3 \times 4{\cdot}42\ \text{A}.$$

In Table 4 are given measurements of $00l$ layers, the average intensities of a layer obtained by estimating the total intensity divided by the number of reflections relative to a maximum equal to 100, the apparent order of the layer, and a calculated value of c_0. Since the measurements of large spacings are not accurate to better than $\pm 3\%$ this value of c_0 is a minimum value only. Thus n_3 is at least 12. Both n_1 and n_2 are probably greater than unity. Rotation photographs of $h00$ and $0k0$ layers were not taken so that n_1 and n_2 were not obtained directly.

Table 4. *Data for phase with composition near* $Ba_2Ni_2O_5$

$d_{\text{meas.}}$	$1/N\ \Sigma I$	l	$c_{0\ \text{calc.}}$
—	100	0	—
13·6	0·5	4	54·4
6·05	1	9	54·5
4·42	30	12	53·1
3·44	0·5	16	55·0
2·56	8	21	53·8
2·215	15	24	53·2
1·906	0·1	28	53·4
1·688	1	31	54·4
1·476	8	36	53·2
1·340	1	40	53·6
1·210	0·3	45	54·5
1·105	3	48	53·1

A rotation photograph of a crystal from a second batch gave a slightly different pattern. How much of the difference was due to differences in dimensions of the crystals and how much to structure was not determined.

Equimolar mixtures of BaO_2 and NiO held in oxygen at temperatures between 750° and 1100° C. yield powdered materials that are hexagonal or very nearly hexagonal, but the powder patterns obtained showed that the materials heated at different temperatures varied slightly in both cell size and location of atoms. Analysis of powders held at temperatures between 750° and 1100° C. revealed that the composition varied in a nearly linear manner from approximately $Ni_4Ba_4O_{11}$ to $Ni_2Ba_2O_5$.

Measurements of a pattern from material with composition near $Ba_3Ni_3O_8$ are given in Table 5. All the reflections are indexed on a hexagonal cell with $a_0 = 5{\cdot}72$ and $c_0 = 4{\cdot}30$ A. The volume of this cell is 122 A.^{3}, or 8 A.^{3} less than that of $BaNiO_3$. It is apparent from the intensities that the barium ions are near $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}; \frac{1}{3}, \frac{2}{3}, \frac{3}{4}$. This places nickel near 0, 0, 0, and 0, 0, $\frac{1}{2}$ with fair probability. It is also apparent (calculated intensities from Table 3 may be used to obtain a good approximation) that either or both of these ions cannot be at exactly these positions. This means that if the pattern is that of a pure phase a larger cell must be chosen and the ions translated in ways appropriate to hexagonal symmetry.

Table 5. *Data for hexagonal phase with composition near* $Ba_3Ni_3O_8$

hkl	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{obs.}}$
101	3·25	3·24	4
110	2·86	2·86	10
200	2·480	2·473	1
111	—	2·380	—
201, 002	2·150	2·144	7
102	1·968	1·966	$\frac{1}{2}$
120	1·871	1·871	$\frac{1}{2}$
121, 112	1·715	1·715	7
300	1·650	1·650	8
202	1·623	1·621	1
301	—	1·540	—
003, 220	1·430	1·429	8
122	1·412	1·410	1
103, 310	1·375	1·373	$\frac{1}{2}$
221	—	1·356	—
311, 302	1·310	1·307	6
113	—	1·278	—
400, 203	1·237	1·237	$\frac{1}{4}$
401, 222	1·190	1·189	4
312	1·157	1·156	$\frac{1}{2}$
320, 123	1·140	1·136	$\frac{1}{2}$
321	1·099	1·097	3
303, 410 402, 004	1·078	1·080 1·073	6
411, 104	—	1·048	—
223 322, 114	1·007	1·010 1·003	$\frac{1}{4}$
313, 500	—	0·990	—
204	—	0·984	—
501, 412	0·966	0·964	2
420, 403	0·937	0·935	$\frac{1}{4}$
331, 124	—	0·931	—
421	0·914	0·915	4
502, 304	—	0·900	—
323, 510	—	0·889	—
511, 332	0·871	0·871	3
600	0·825	0·825	2
520, 333	0·793	0·793	4

Since it is possible that none of the materials is a pure phase, since there are at least several space groups to which each of the compounds $Ba_2Ni_2O_5$, $Ba_3Ni_3O_8$, etc., may plausibly belong, and since many types of reflections overlap in the powder patterns, a convincing complete structure analysis has not been obtained.

Summary of compounds with composition near $Ba_2Ni_2O_5$:

Hexagonal and pseudo-hexagonal orthorhombic with a_0 near $n_1 \times 5{\cdot}72$ A. and c_0 near $n_3 \times 4{\cdot}35$ A.

Barium ions in close-packed hexagonal arrangement.

Nickel ions probably near 0, 0, 0; 0, 0, ½ in the basic cell.

Oxygen arrangement unknown.

Number and exact oxygen content of stable phases unknown. Disorder in oxygen probably prevalent in the material obtained in powder form.

Relations among the structures $BaNiO_x$

The arrangement of ions in the structure assigned to $BaNiO_2$ may be obtained by removing oxygen symmetrically (octahedral arrays go to square arrays) from that assigned to $BaNiO_3$. The resultant cell was found to be orthorhombic, but nearly hexagonal. For the structures $BaNiO_x$ with x between 2 and 3 the same close-packed hexagonal arrangement of Ba ions was deduced, and Ni ions probably have not been grossly displaced. The data seem to indicate that various intricate orderings of oxygen ions appear.

Unknown phase

The final phase to be reported is an unknown that was obtained when two or more moles of BaO_2 were mixed with one mole of NiO and the mixture was heated to about 1000° C. in nitrogen containing about 1% oxygen. The unknown phase, like NiO.3BaO, is soluble in alkali and therefore not easily separated from BaO, with which it was found in several attempts to prepare it pure. Its composition is $Ba_2Ni_xO_y$ in which $x=1$–2 and $y=4$–5. Results from the measurement of the best pattern are given in Table 6, and they are believed to include only the unknown phase.

Table 6. *Data for unknown phase in* Ni–Ba–O *system*

d (A.)	$I_{\text{obs.}}$	d (A.)	$I_{\text{obs.}}$
3·20	7	1·755	2
3·07	10	1·643	1
2·58	3	1·612	2
2·47	8	1·422	2
2·32	4	1·400	2
1·912	2	1·200	½
1·865	1	1·150	1
1·803	1		

Bond types from the structures and available magnetic data

Structural and magnetic data should lead to the assignment of the configurations of the nickel valence electrons for the compounds reported. The assumptions made are that bonds between nickel and oxygen have a large amount of covalent character and that the configurations assumed by the oxygen ions around nickel positively identify valence orbitals used in the structure (Pauling, 1939, chap. 3). The nickel ion Ni^{++} has two unpaired electrons and an observable magnetic moment. The nickel ion Ni^{4+} would have four unpaired electrons and a magnetic moment equal to approximately twice that of Ni^{++}. However, these ions are not to be expected in the compounds under discussion. Rather, it is to be expected that nickel will share electrons with oxygen and the magnetic moment of the compound will depend on the type of co-ordination.

In the first compound described, NiO.3BaO, it was deduced that nickel is surrounded by three oxygen ions in a coplanar triangular arrangement. Although this is probably the first example of such behavior by nickel, nevertheless, there appears to be no cause for alarm. Coplanar triangular co-ordination is well known and Pauling (1939, p. 88) calculates that the bond strength of the three hybridized orbitals sp^2 which may produce coplanar triangular co-ordination should be only slightly less than that of tetrahedral orbitals. Formation of sp^2 bonds leaves two of the d electrons of nickel unpaired, therefore a magnetic moment approaching that of two unpaired electrons per nickel atom should be observed. Magnetic susceptibility measurements have not been made because of the instability of the compound.

In the compound $BaNiO_3$ octahedral co-ordination of oxygen by nickel was observed. This should correspond to the formation of the six bonds d^2sp^3 between six oxygen ions and a nickel ion with sufficient electrons to fill three of the $3d$ orbitals. This leaves no unpaired electrons. Magnetic susceptibility measurements gave a moment corresponding to 0·8 unpaired electron. Since the use of higher orbitals would result in large instability the cause of the observed moment is probably to be found in partial ionic character of the bonds.

One of the intermediate compounds, with formula near $Ba_2Ni_2O_5$ was found to have a magnetic moment corresponding to approximately 1·0 unpaired electrons. Since the type of co-ordination of oxygen was not determined, grounds for assigning an electron configuration are dubious.

The compound NiO.BaO was found to have a square coplanar co-ordination of oxygen by nickel. Now this co-ordination results from the formation of four covalent dsp^2 bonds and for bivalent nickel this leaves no unpaired electrons. But a magnetic moment corresponding to 1·8 unpaired electrons was observed. This large magnetic moment may be due either to practically pure ionic character of bonds or to additional bonding in the compound. Evidence seems to favor the theory of an additional bond. Nickel is not expected to form purely ionic bonds in these compounds, the square co-ordination is indicative of covalent bonds, the linear arrangement of nickel ions with the rather short Ni–Ni distance of 2·36 A. is suggestive of a Ni–Ni bond, and finally one of the p orbitals of the ion is not used in the dsp^2 configuration. To use this third $4p$ orbital two electrons must be promoted from the $3d$ shell and this leaves two unpaired electrons in the $3d$ shell. The vacancies, which if filled by oxygen would produce oxygen octahedra, are likely regions for concentration of extra electronic charge.

A note about NiO

It is well known that NiO can be made with a very large stoichiometric excess of oxygen, and quantitative determinations of this excess can be made. Existence of the higher oxides Ni_3O_4, Ni_2O_3 and even NiO_2 has been proposed. However, X-ray diffraction patterns obtained from these higher oxides do not reveal a structure different from that of NiO. They do indicate that with increasing state of oxidation the materials become increasingly amorphous.

A possibly related problem is how does bivalent nickel in pure NiO co-ordinate oxygen octahedrally. It has two too many electrons to form six d^2sp^3 bonds. One is therefore led to investigate the possibility of resonating structures. A square co-ordinated complex of dsp^2 bonds with partial ionic character resonating among the three possible square configurations about nickel would account for the observed magnetic moment corresponding to approximately 0·8 unpaired electrons. Removal of a nickel atom from the crystal removes two electrons from the crystal. These presumably are supplied by one or two of the nickel ions nearest the vacant lattice site with the production of higher valent nickel and an approach to the formation of d^2sp^3 bonds. Equilibrium concentrations of interior lattice vacancies are not known but obviously in the extreme oxide (with composition near NiO_2) most of the vacant lattice sites must be on the crystal boundaries; that is to say, the crystal tends toward the amorphous state.

Much of the above work followed suggestions made by others at these laboratories. In particular the author wishes to acknowledge F. Morin (who also contributed measurements of magnetic susceptibilities), L. Wooten, K. Storks, Mrs E. A. Wood, and P. Anderson.

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The Structure of Millon's Base and its Salts

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The structure of Millon's base, $Hg_2NOH.2H_2O$, consists of a three-dimensional framework Hg_2N^+ in an idealized cristobalite type of arrangement. The mercury atoms form linear *sp* bonds, while the nitrogen forms tetrahedral sp^3 bonds, in a face-centered cubic lattice with $a = 9{\cdot}58$ A. The Hg–N bond distance is $2{\cdot}07_3$ A.

In the course of a study of reactions between mercury (I) compounds and ammonia (Arora, Lipscomb & Sneed, 1951), a sample of Millon's base, $Hg_2NOH.2H_2O$, was prepared. A powder diffraction pattern was taken, and has now been analyzed to yield the essentials of the structure of this compound.

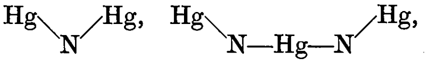
Experimental results

The sample was placed inside a pyrex capillary about 0·2 mm. in diameter, and powder photographs were taken in a cylindrical camera of 5·73 cm. radius. Integrated intensities of the lines were estimated by a combination of micro-photometer tracings and visual estimates, and corrections were applied to these intensities, but not to the spacings, for the effect of absorption by the sample (*Internationale Tabellen*, 1935, vol. 2, p. 583).

Because initial attempts to index the pattern failed, a radial distribution function was prepared. The expression (Waser & Schomaker, 1945)

$$rD(r) = \sum_i \frac{I_i \sin 2\theta_i}{1+\cos^2 2\theta_i} \exp\left[-3\frac{\sin^2\theta_i}{\lambda^2}\right] \sin 2\pi h_i r,$$

where $h_i = 2\sin\theta_i/\lambda$, was summed at intervals of 0·1 A. in r to give the result shown in Fig. 1. The function shows three clearly resolved peaks at 3·4, 5·9 and 6·9 A. These distances are nearly what would be expected from Hg...Hg distances in the configurations



and