Oxide Chemistry. Part I. Ternary Oxides containing Nickel in Oxidation States II, III, and IV

By Miss Mehran Arjomand and David J. Machin,* Department of Chemistry, The University, Manchester M13 9PL

Attempts to resolve differences in the literature concerning the structures and magnetic properties of the compounds $BaNiO_2$ and $BaNiO_3$ are reported. $BaNiO_2$ has the properties of an octahedral nickel(II) compound ($SrNiO_2$ cannot be obtained free from NiO). Nickel(III) systems, A_2NiO_4 (A = La, Al, or Ga), have also been prepared. Equilibria in the $BaNiO_2 \rightleftharpoons BaNiO_{2.5} \rightleftharpoons BaNiO_3$ system have been studied by thermogravimetric analysis: there is a continuous variation of composition with temperature, at least between the latter two members. $LaNiO_3$ and $YNiO_3$ are also described. Magnetic susceptibilities from 80 to 300 K are reported for all compounds.

ALTHOUGH many compounds which contain nickel(II) are known, very little is known of the chemistry of the metal in higher oxidation states. Thus nickel(III) is found in substituted phosphine complexes of the type $[NiX_3(PR_3)_2]$ and in various oxide hydroxides, *e.g.* NiO(OH). Nickel(IV) is found as periodates such as $Na(K)[NiIO_6]\cdot nH_2O$ and in $K_2[NiF_6]$ as well as in heteropoly-molybdates and -niobates. Apart from these, a number of ternary-oxide phases, discussed below, have been reported to contain nickel-(III) or -(IV).

The presence of higher oxidation states of nickel in oxide systems was first shown by Thurber [1] in reactions between NiO and $BaCO_3$, although the product was not fully characterised. Lander [2-4] has described the formation of $BaNiO_2$ and $BaNiO_3$ as well as intermediate phases $BaNiO_{2.5}$ and $BaNiO_{2.66}$. Lander interprets his *X*-ray powder data in terms of square planar co-ordination of nickel(II) in $BaNiO_2$. This is hard to reconcile with his report that its magnetic moment at room temperature is 2·6 B.M. since square planar d^8 systems are normally diamagnetic.† $BaNiO_3$ has a distorted perovskite structure containing chains of octahedra sharing faces. Lander reports μ_{eff} = 1·5 B.M. for this compound, which might also be expected to be diamagnetic (*i.e.* low spin d^6). Subsequently, both compounds have been reported [5,6] to be diamagnetic as

† 1 B.M. ≈ 9·27 × 10^{-24} A m².

[1] E. A. Thurber and B. Ormont, *J. Gen. Chem. (U.S.S.R.)*, 1938, **8**, 563.
[2] J. J. Lander, *Acta Cryst.*, 1959, **4**, 148.
[3] J. J. Lander, *J. Amer. Chem. Soc.*, 1951, **73**, 2450.
[4] J. J. Lander and L. A. Wooten, *J. Amer. Chem. Soc.*, 1951, **73**, 2452.
[5] H. Krischner, K. Torkar, and B. O. Kolbeson, *J. Solid State Chem.*, 1971, **3**, 349.
[6] A. Almodovar, H. J. Bielen, B. C. Frazer, and M. I. Kay, *J. Phys. (Paris)*, 1964, **25**, 442.

would be expected. It is still somewhat surprising to find square planar co-ordination in a compound of this type. Thermogravimetric studies [5,6] of $BaNiO_2$ have also appeared. Of the intermediate phases reported by Lander, $BaNiO_{2\cdot5}$ has the correct composition to contain nickel(III); however it is not isostructural with the $BaNiO_3$ described in the same paper. The reported paramagnetism of the last compound casts some doubt upon its formulation. $SrNiO_3$ and $SrNiO_{2\cdot5}$ are the only other similar compounds which have been described.[7]

Nickel(III) may also be stabilised in a perovskite-type lattice without oxygen deficiency by changing from barium to a suitably sized trivalent ion. Compounds $ANiO_3$, A = Y [8,9] and La,[10,11] have been prepared. When A is Al,[12-14] Ga,[15,16] or La,[17] the nickel(II) phases A_2NiO_4 can also be obtained.

We report here attempts to clarify and extend knowledge of the oxide chemistry of nickel.

RESULTS AND DISCUSSION

(a) *Nickel*(II) *Compounds*.—$BaNiO_2$ is best prepared by heating an equimolar mixture of BaO and NiO *in vacuo* at 980 °C for *ca*. 30 h. It is essential to exclude oxygen, and some care is needed in the choice of conditions. Thus our initial preparations in a continuously evacuated silica tube or in a helium atmosphere in a nickel tube both led to the formation of nickel in the product, detectable by its *X*-ray powder pattern. In both cases this is due to dissociation of the nickel oxide, the oxygen being pumped away, or attacking the tube respectively. The best procedure is to seal the reactants in a platinum capsule and to heat in an evacuated silica tube. Preparations under these conditions had the *X*-ray pattern reported by Lander [2-4] and contained no reflections attributable to starting materials or to metallic nickel. The very small field-dependence of the magnetic susceptibility of our preparation also indicates the absence of metallic nickel. The *X*-ray powder data are in Table 1. It may be that some of the confusion over magnetic data is attributable to the presence of metallic nickel in various preparations. We are confident that our samples are not contaminated in this way.

$BaNiO_2$ is a black microcrystalline material which is soluble in hydrochloric acid. It does not release iodine when dissolved in acidified potassium iodide solution which confirms the presence of nickel(II). Analyses (see Table 2) are also consistent with the formulation $BaNiO_2$ although the barium and nickel analyses are not very sensitive to composition when comparing, for example, $BaNiO_2$ and $BaNiO_3$. The magnetic properties of $BaNiO_2$ are summarised in Table 3; details are in Table 4. The room-temperature magnetic moment (3·14 B.M.) is close to that expected for octahedrally co-ordinated nickel(II), *e.g.* $\mu_{eff} \simeq 3{\cdot}1$ B.M. for hexa-aquanickel(II) salts, with a small Weiss constant, θ. This is in contrast with Lander's structural conclusions

TABLE 1

X-Ray powder pattern of $BaNiO_2$

h	*k*	*l*	d_{obs}	d_{cal}	I_{obs}
0	2	0	4·57	4·59	5
1	1	1	3·40	3·41	100
0	2	1	3·31	3·31	25
2	0	0	2·86	2·86	30
1	3	0	2·70	2·70	95
0	0	2	2·391	2·390	15
1	3	1	2·347	2·351	<5
0	4	0	2·292	2·296	5
2	2	1	2·163	2·165	80
1	1	2	2·146	2·145	55
0	2	2	2·117	2·120	20
0	4	1	2·069	2·070	30
2	0	2	1·833	1·835	5
1	3	2	1·788	1·790	10
3	1	1	1·736	1·740	25
2	2	2	1·707	1·704	30
2	4	1	1·675	1·677	10
0	4	2	1·656	1·656	25
1	5	1	1·639	1·643	30
3	3	0	1·618	1·619	35
0	6	0	1·533	1·531	10
1	1	3	1·511	1·514	15
0	2	3		1·506	5
3	1	2	1·470	1·472	20
2	4	2	1·432	1·433	35
4	0	0		1·431	
1	5	2	1·411	1·412	10
2	6	0	1·351	1·350	20
3	3	2	1·340	1·341	5
4	2	1	1·314	1·313	10
0	4	3	1·309	1·309	5
3	5	1	1·275	1·275	20
1	7	1	1·236	1·236	10
4	0	2	1·228	1·228	<5
3	1	3	1·214	1·212	5
0	0	4	1·195	1·195	15
4	2	2	1·185	1·186	
1	5	3	1·177	1·178	15
4	4	1		1·177	
2	6	2		1·175	
3	5	2	1·158	1·158	10

since all known square-planar nickel(II) compounds are diamagnetic. There must be fairly large uncertainties in oxygen positions determined from *X*-ray powder data in compounds of this type. At the same time, we disagree with Krishner *et al*.[5] who found the compound to be diamagnetic. Our results are reproducible over a number of separate preparations and the absence of field-dependence of the susceptibility rules out the presence of nickel metal in our preparations; neither can any other paramagnetic impurity be detected in the *X*-ray powder pattern.

[7] Y. Takeda, T. Hashino, H. Miyamoto, F. Kanamaru, S. Kume, and M. Hoizume, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1599.
[8] G. Demazeau, A. Marbeuf, M. Pouchard, P. Hagenmuller, and J. B. Goodenough, *Compt. rend.*, 1971, **272**, 2163.
[9] G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.*, 1971, **3**, 582.
[10] A. Wold and R. J. Arnott, *J. Phys. and Chem. Solids*, 1959, **9**, 176.
[11] A. Wold, B. Post, and E. Bank, *J. Amer. Chem. Soc.*, 1957, **79**, 4911.
[12] S. Greenwald, S. J. Pickart, and F. H. Grannis, *J. Chem. Phys.*, 1954, **22**, 1597.
[13] A. Navrotsky and O. J. Kleppa, *J. Inorg. Nuclear Chem.*, 1968, **30**, 479.
[14] G. E. Bacon and F. F. Roberts, *Acta Cryst.*, 1953, **6**, 57.
[15] S. A. Panakh-Zade, V. F. Plyuschev, and M. B. Vorflomeev, *Zhur. neorg. Khim.*, 1970, **15**, 1702.
[16] J. Goffin, N. Baffier, and M. Huber, *Compt. rend.*, 1961, **252**, 2744.
[17] A. Rabenau and P. Eckerlin, *Acta Cryst.*, 1958, **11**, 304.

We have been unable to prepare $SrNiO_2$ free from unchanged NiO. The room-temperature magnetic moment is 2·98 B.M.: although there is some uncertainty in this figure because of the presence of small amounts of NiO, there is a general similarity with $BaNiO_2$. If reflections due to NiO are neglected, the *X*-ray powder patterns of $BaNiO_2$ and $SrNiO_2$ show them to be isostructural. All attempts to prepare calcium or magnesium analogues failed.

TABLE 2

Analytical data (the proportion of oxygen in the formulae listed has been calculated from the mean oxidation state of the nickel, determined analytically)

Compound	Calculated composition %A	Calculated composition %Ni	Found composition %A	Found composition %Ni
$SrNiO_{2\cdot0}$	49·13	32·92	48·2	33·6
$SrNiO_{2\cdot5}$	47·02	31·51	46·9	31·8
$SrNiO_{2\cdot59}$	46·66	31·27	46·9	31·6
$SrNiO_{2\cdot90}$	45·46	30·46	45·2	30·4
$SrNiO_{3\cdot0}$	45·09	30·21	45·4	30·6
$BaNiO_{2\cdot0}$	60·22	25·74	59·9	25·9
$BaNiO_{2\cdot36}$	58·74	25·11	58·5	25·4
$BaNiO_{2\cdot5}$	58·18	24·87	57·9	25·2
$BaNiO_{2\cdot57}$	57·91	24·75	57·9	24·9
$BaNiO_{2\cdot69}$	57·44	24·56	57·6	24·8
$BaNiO_{2\cdot78}$	57·10	24·41	57·5	24·1
$BaNiO_{2\cdot85}$	57·83	24·30	56·8	24·4
$BaNiO_{2\cdot92}$	56·57	24·18	56·4	24·3
$BaNiO_{3\cdot0}$	56·27	24·06	56·6	24·4
$YNiO_{3\cdot0}$	45·43	30·00	45·3	30·4
$LaNiO_{3\cdot0}$	56·55	23·90	56·3	23·6
$La_2NiO_{4\cdot0}$	69·36	14·66	69·2	14·8
$Al_2NiO_{4\cdot0}$	30·54	33·23	32·7 ± 1	31·8
$Ga_2NiO_{4\cdot0}$	53·19	22·39	52·8	23·5

TABLE 3

Magnetic properties of nickel ternary oxides

Compound	μ_{eff}/B.M. 300 K	μ_{eff}/B.M. 80 K	θ/K	Range * K	% Field dependence † 300 K	% Field dependence † 80 K
$SrNiO_2$	2·98					
$SrNiO_{2\cdot5}$	1·55	0·89	1 150	200	0·8	1·0
$SrNiO_{2\cdot59}$	1·64	1·25	230	200	0·0	0·2
$SrNiO_{2\cdot90}$	1·74	1·76	0	80	0·0	0·0
$SrNiO_3$	0·0	0·0				
$BaNiO_2$	3·14	2·77	35	80	0·2	0·5
$BaNiO_{2\cdot36}$	1·23	0·61			0·0	0·0
$BaNiO_{2\cdot5}$	1·56	1·01	550	180	0·7	1·2
$BaNiO_{2\cdot57}$	1·61	1·13	200	150	0·4	0·9
$BaNiO_{2\cdot69}$	1·71	1·49	45	80	0·2	0·6
$BaNiO_{2\cdot78}$	1·76	1·67	15	80	0·2	0·7
$BaNiO_{2\cdot85}$	1·79	1·75	5	80	0·0	0·3
$BaNiO_{2\cdot92}$	1·79	1·76	5	80	0·0	0·0
$BaNiO_3$	0·0	0·0				
$YNiO_3$	1·79	1·00	190	200	0·0	0·0
$LaNiO_3$	1·75	0·95	3 700	120	2·0	6·0
La_2NiO_4	1·70	1·09	790	230	0·0	0·0
Al_2NiO_4	2·67	2·51	20	80	0·0	0·0
Ga_2NiO_4	3·13	3·16	5	80	0·0	0·0

* A Curie–Weiss law is obeyed above this temperature. † Difference between susceptibilities measured at 4 950 and 6 050 Oe.

The only other nickel(II) compounds which we have been able to isolate are the previously known phases A_2NiO_4 (A = La, Al, or Ga). These are best prepared from the oxides or nitrates at 1 100 °C for 30 h, 950 °C for 48 h, and 1 150 °C for 7 days respectively. The nickel analysis of Al_2NiO_4 (see Table 2) is rather low, perhaps due to the volatility of the $Ni(NO_3)_2$ used in the preparation. The structure of La_2NiO_4 is similar to that of K_2NiF_4, while the aluminium and gallium compounds are spinels. The unit-cell dimensions and symmetries are listed in Table 5.

The magnetic susceptibility of La_2NiO_4 (see Tables 3 and 4) obeys a Curie–Weiss law above *ca.* 200 K with a very large positive Weiss constant, θ. Below *ca.* 200 K the value of $1/\chi$ drops more rapidly than expected and appears to be approaching a minimum (*i.e.* the Néel point). The susceptibility is not field dependent. Although there is no direct indication of antiferromagnetism, these observations suggest that such an interaction does occur below 80 K. Compounds with the K_2NiF_4 layer structure are commonly antiferromagnetic. In

TABLE 4

Magnetic susceptibilities of nickel ternary oxides as a function of absolute temperature (susceptibility measurements are at 6 050 Oe)

$SrNiO_{2\cdot50}$ T	$SrNiO_{2\cdot50}$ $1/\chi_{Ni}$	$SrNiO_{2\cdot59}$ T	$SrNiO_{2\cdot59}$ $1/\chi_{Ni}$	$SrNiO_{2\cdot90}$ T	$SrNiO_{2\cdot90}$ $1/\chi_{Ni}$	$BaNiO_2$ T	$BaNiO_2$ $1/\chi_{Ni}$
309·8	1 015	305·3	909	309·0	820	301·6	242
299·2	1 000	296·8	893	300·2	787	290·0	231
286·5	1 000	283·0	870	290·8	763	278·4	227
274·9	990	275·0	855	283·1	746	267·5	217
265·4	980	262·9	840	272·0	714	255·6	210
256·1	971	254·1	826	261·3	690	247·5	202
244·3	962	245·5	800	249·7	662	236·8	195
232·0	962	234·2	787	239·4	630	226·5	195
220·7	952	225·7	775	228·1	602	217·6	180
210·6	943	217·0	752	220·0	571	207·4	174
201·5	935	207·3	740	210·4	559	197·3	163
193·4	926	196·4	714	201·6	523	187·7	160
181·1	909	187·6	704	191·2	505	178·4	151
178·8	893	178·0	685	179·5	463	167·3	143
159·2	877	170·1	667	168·1	442	156·9	134
148·5	847	161·2	641	157·9	406	146·0	127
137·2	820	149·5	613	149·6	394	137·6	120
130·0	794	138·0	588	141·5	369	125·4	114
118·9	763	125·7	552	130·0	331	111·9	104
108·3	735	114·1	518	119·2	310	100·3	97·3
99·5	719	107·2	497	108·0	277	89·5	88·1
88·3	699	96·0	465	97·5	251	79·2	82·3
79·1	685	86·8	435	88·3	228		
		78·6	405	78·4	205		

$BaNiO_{2\cdot36}$ T	$BaNiO_{2\cdot36}$ $1/\chi_{Ni}$	$BaNiO_{2\cdot50}$ T	$BaNiO_{2\cdot50}$ $1/\chi_{Ni}$	$BaNiO_{2\cdot57}$ T	$BaNiO_{2\cdot57}$ $1/\chi_{Ni}$	$BaNiO_{2\cdot69}$ T	$BaNiO_{2\cdot69}$ $1/\chi_{Ni}$
304·9	1 587	295·8	971	307·3	934	306·3	833
294·2	1 613	283·6	962	298·0	917	299·0	813
285·2	1 652	274·0	962	288·9	901	290·1	793
277·6	1 724	264·3	943	281·5	893	280·9	769
267·7	1 754	255·5	935	272·1	877	273·0	757
255·7	1 852	246·5	926	263·4	855	265·3	730
245·2	1 869	237·0	917	254·0	840	256·2	709
237·5	1 923	225·5	901	243·2	833	247·8	699
227·8	2 000	214·9	885	232·0	806	239·5	671
216·8	2 041	205·3	877	222·7	793	230·2	649
205·8	2 000	194·8	862	214·1	775	222·0	629
195·2	2 105	184·2	847	205·5	763	211·1	602
184·7	2 083	172·6	833	195·3	741	202·7	592
172·1	2 127	160·5	813	186·0	725	191·6	555
162·5	2 105	146·9	787	176·6	709	181·2	532
146·8	2 083	133·3	763	165·4	680	170·0	510
132·7	2 041	118·2	735	153·8	667	161·9	488
116·3	1 980	102·5	694	143·1	645	150·4	463
99·7	1 869	91·1	662	129·2	610	138·3	438
81·5	1 754	79·3	621	117·7	588	127·1	402
				107·3	562	119·5	382
				98·5	540	108·9	357
				88·2	518	97·4	332
				78·4	490	88·1	306
						78·5	299

Table 4 (*Continued*)

$BaNiO_{2\cdot78}$ T	$1/\chi_{Ni}$	$BaNiO_{2\cdot85}$ T	$1/\chi_{Ni}$	$BaNiO_{2\cdot92}$ T	$1/\chi_{Ni}$	$YNiO_3$ T	$1/\chi_{Ni}$
302·0	787	305·1	769	312·0	787	308·3	763
294·2	757	296·0	746	300·5	752	297·8	746
283·5	730	285·5	719	290·2	725	288·1	730
275·0	714	273·8	690	279·4	709	276·9	714
266·9	694	264·0	658	265·6	680	266·5	699
259·1	671	257·0	645	257·9	645	257·2	680
250·3	653	245·3	621	247·5	617	248·0	667
240·8	629	232·1	592	236·0	599	238·4	654
230·2	599	221·5	559	226·1	571	228·9	641
222·4	578	210·2	532	211·8	538	210·0	613
209·7	549	199·9	508	197·3	495	200·9	599
198·0	508	189·5	481	185·1	467	189·8	588
187·1	490	179·0	457	174·5	444	179·6	571
175·9	476	166·7	424	163·4	410	168·7	565
164·4	439	158·1	400	150·7	383	158·9	559
155·0	417	146·0	369	137·6	355	147·3	559
143·7	383	134·0	345	130·0	327	138·0	565
133·3	369	125·2	320	120·5	306	127·9	575
125·6	342	112·8	296	110·1	285	117·5	585
112·9	310	101·3	264	100·3	268	108·4	595
106·0	293	89·6	234	91·3	241	99·5	613
98·5	276	78·4	201	78·9	202	89·6	625
87·3	247					79·0	641
78·0	224						

$LaNiO_3$ T	$1/\chi_{Ni}$	La_2NiO_4 T	$1/\chi_{Ni}$	Al_2NiO_4 T	$1/\chi_{Ni}$	Ga_2NiO_4 T	$1/\chi_{Ni}$
304·2	781	303·8	833	306·4	342	311·7	255
294·7	778	294·0	826	298·0	334	301·8	243
285·1	775	283·0	820	289·6	326	292·4	236
276·4	778	274·7	813	281·2	317	284·3	229
267·7	775	267·7	806	272·7	310	274·8	222
258·8	772	259·5	800	264·0	302	266·1	215
250·9	772	250·9	794	256·1	293	257·9	208
242·2	769	242·8	794	248·5	285	248·6	198
234·0	766	234·2	781	240·5	275	240·2	193
225·5	763	225·2	775	231·9	267	231·7	185
216·6	763	215·8	769	223·3	257	222·8	177
207·6	760	205·4	758	214·2	249	214·1	169
198·5	760	196·3	746	205·5	239	205·3	161
189·4	759	186·9	735	196·2	229	194·7	152
178·8	757	175·1	719	186·4	219	184·2	144
166·9	756	163·4	704	176·3	207	173·1	135
155·7	755	151·5	680	165·3	196	162·0	127
143·7	752	137·0	649	154·9	185	150·8	119
132·6	749	123·4	613	143·6	172	139·3	110
118·6	746	108·3	581	132·6	160	127·0	98·1
105·0	743	94·2	555	120·5	147	117·6	91·6
92·8	738	78·4	538	106·5	133	106·4	82·5
83·0	730			92·9	119	97·4	76·2
				80·2	102	87·5	69·3
						77·8	62·6

contrast, the spinels Al_2NiO_4 and Ga_2NiO_4 show much simpler magnetic properties. Both obey Curie–Weiss laws down to 80 K with small θ values. The magnetic moment of Al_2NiO_4 is somewhat smaller than might be expected but Ga_2NiO_4 behaves as expected for an ion with the $^3A_{2g}$ ground term arising from octahedral nickel(II) (see Tables 3 and 4). The aluminium compound has the larger θ, and this would be expected since any interaction will be the greatest for the compound with the smallest unit cell.

Site-preference energy considerations lead one to expect that nickel(II) will occupy octahedral sites in the spinel structure. This is supported by the magnetic data and also by the electronic spectra. These are the only nickel compounds studied which were not black. The reflectance spectra of these green solids are given in Table 6. Both can be satisfactorily assigned on the basis of octahedral d^8 systems, the spin-forbidden bands helping to confirm the assignment in the case of Al_2NiO_4. As would be expected, the Racah parameter, B, is about the same for both compounds. The crystal-field parameter, Dq, is greater for the aluminium compound again as would be expected as its unit cell is the smaller (Table 5). It is not possible to give extinction coefficients for the bands as these are reflectance spectra, however, those assigned to spin-forbidden transitions were weaker.

Table 5

The symmetry and unit-cell dimensions of nickel ternary oxides

Compound	Symmetry	a/Å	b/Å	c/Å
$SrNiO_2$	Orthorhombic	5·55	9·02	4·63
$SrNiO_{2\cdot5}$	Hexagonal	5·41		4·61
$SrNiO_{2\cdot59}$	Hexagonal	5·40		4·61
$SrNiO_{2\cdot90}$	Hexagonal	5·35		4·58
$SrNiO_3$	Hexagonal	5·33		4·57
$BaNiO_2$	Orthorhombic	5·72	9·18	4·78
$BaNiO_{2\cdot36}$	Hexagonal	5·72		4·29
$BaNiO_{2\cdot5}$	Hexagonal	5·59		4·84
$BaNiO_{2\cdot57}$	Hexagonal	5·59		4·84
$BaNiO_{2\cdot69}$	Hexagonal	5·58		4·83
$BaNiO_{2\cdot78}$	Hexagonal	5·56		4·82
$BaNiO_{2\cdot85}$	Hexagonal	5·54		4·81
$BaNiO_{2\cdot92}$	Hexagonal	5·53		4·80
$BaNiO_3$	Hexagonal	5·51		4·79
$YNiO_3$	Orthorhombic	5·18	5·54	7·45
$LaNiO_3$	Hexagonal	5·45		13·12
La_2NiO_4	Tetragonal	3·87		12·67
Al_2NiO_4	Cubic	8·05		
Ga_2NiO_4	Cubic	8·26		

(b) *Nickel*(III) *Compounds*.—$BaNiO_{2\cdot5}$ and $SrNiO_{2\cdot5}$ were made by heating BaO_2 and NiO or $Sr(NO_3)_2$ and $Ni(NO_3)_2$ for 24 h in air at 700 and 670 °C respectively. The temperature at which the preparation is carried out is quite critical as will be seen in the discussion of the decomposition of $BaNiO_3$ in section (c). The mean oxidation state of the nickel, determined analytically, is very close to III (see Table 2). This does not positively exclude the existence of an equimolar mixture of nickel(II) and nickel(IV), and the *X*-ray powder pattern is identical with that of $BaNiO_3$, in contrast to Lander's observation, so that the presence of nickel(IV) cannot be excluded. *X*-Ray evidence is that any nickel(II) certainly does not occur as $BaNiO_2$. The possibility of equal numbers of nickel-(II) and -(IV) is unlikely for several reasons. (i) It is unlikely that two ions of very different sizes would be accommodated in the lattice without producing some distortion. (ii) If the site occupancy were random, then since Ni^{IV} ions will certainly be diamagnetic, the magnetic behaviour is likely to be that of a magnetically dilute system whereas both compounds show evidence of antiferromagnetism. (iii) Having regard to the observed values of θ, μ_{eff} is appropriate to a low-spin d^7 system. The magnetic susceptibilities of both the barium and strontium compounds obey Curie–Weiss laws above 200 K with positive θ values. Although no minimum is observed in the plot of $1/\chi$, antiferromagnetic ordering is suggested. In neither case is the susceptibility strongly field dependent.

When heated in a muffle furnace at 900 °C, $BaNiO_{2\cdot5}$ decomposes, forming a phase of composition $BaNiO_{2\cdot36}$. Studies under more carefully controlled conditions, using a thermobalance, show that the equilibrium compositions are very temperature-dependent. The following data were obtained heating a sample slowly (*ca.* 0·5 °C min^{-1}) in air to the stated temperature and then holding that temperature until there was no further weight loss (*ca.* 12 h). Compositions are calculated assuming that all of the weight loss was due to oxygen.

TABLE 6

Reflectance spectra of Al_2NiO_4 and Ga_2NiO_4

Al_2NiO_4 Transition	E_{cal}/cm^{-1}	E_{obs}/cm^{-1}	Ga_2NiO_4 Transition	E_{cal}/cm^{-1}	E_{obs}/cm^{-1}
$^3A_{2g} \longrightarrow {}^3T_{2g}$	9 790	9 820	$^3A_{2g} \longrightarrow {}^3T_{2g}$	9 090	9 310
$^3A_{2g} \longrightarrow {}^3T_{1g(F)}$	16 480	16 130	$^3A_{2g} \longrightarrow {}^3T_{1g(F)}$	16 300	15 810
$^3A_{2g} \longrightarrow {}^1E_{g(D)}$	17 720	18 050	$^3A_{2g} \longrightarrow {}^3T_{1g(P)}$	25 600	25 740
$^3A_{2g} \longrightarrow {}^1T_{1g(D)}$	25 850	23 800			
$^3A_{2g} \longrightarrow {}^3T_{1g(P)}$	28 740	28 570			

$Dq = 980\ cm^{-1}$; $B = 1\ 030\ cm^{-1}$ (Al₂NiO₄) $Dq = 931\ cm^{-1}$; $B = 1\ 045\ cm^{-1}$ (Ga₂NiO₄)

t/°C	700	750	800	850	900	950
x in $BaNiO_x$	2·5	2·49	2·47	2·44	2·25	2·19

There is some oxygen uptake on cooling to 400 °C in air, the final composition being $BaNiO_{2\cdot44}$.

Our preparation of $BaNiO_{2\cdot36}$ has an X-ray pattern similar to that of Lander's $BaNiO_{2\cdot66}$ and was indexed with a hexagonal unit cell (see Tables 5 and 7). The mean oxidation state determined analytically and the analytical data (Table 2) support the presence of 72% nickel(III) in this material.

The temperature variation of the susceptibility of this compound is very strange. The *inverse* susceptibility shows a very broad maximum. The only common reason for such an observation is when an antiferromagnetic substance with Néel point above room temperature is contaminated with a normal paramagnetic species. The X-ray pattern (Table 7) seems to exclude this in this instance.

TABLE 7

X-Ray powder pattern of $BaNiO_{2\cdot36}$

$h\ k\ l$	d_{obs}	d_{cal}	I_{obs}	$h\ k\ l$	d_{obs}	d_{cal}	I_{obs}
1 0 1	3·26	3·24	45	2 0 2	1·627	1·622	15
1 1 0	2·86	2·86	100	0 0 3	1·429	1·431	80
2 0 0	2·48	2·48	10	2 2 0		1·430	
0 0 2	2·148	2·147	75	3 1 1	1·309	1·310	55
2 0 1		2·146		3 0 2		1·309	
1 0 2	1·975	1·970	5	4 0 1	1·190	1·190	35
1 1 2	1·717	1·717	70	2 2 2		1·189	
1 2 1		1·716		3 2 1	1·099	1·099	30
3 0 0	1·651	1·651	85				

We have also prepared $YNiO_3$ and $LaNiO_3$ since these should only contain nickel(III). We were unable to prepare the scandium, aluminium, or gallium analogues. The X-ray pattern of $YNiO_3$ is listed in Table 8 since it was not recorded in previous reports:[8,9] we found an identical unit cell. In the case of $LaNiO_3$, although we observed an identical X-ray pattern,[10,11] we could only index it by doubling c.

The yttrium compound is antiferromagnetic with a Néel temperature of 150 K. Its susceptibility obeys a Curie–Weiss law above 200 K, with positive θ as would be expected. Although $LaNiO_3$ has a large positive θ, no Néel temperature was observed down to 80 K. The value of μ_{eff} is appropriate to a low-spin d^7 ion, but the susceptibility becomes increasingly field dependent as the temperature is lowered.

$YNiO_3$ cannot be formed at atmospheric pressure: it was prepared from Y_2O_3 and NiO in oxygen at 400 atm and 1 000 °C for 12 h. $LaNiO_3$ is formed from the oxides heated in air at 800 °C in a flux of Na_2CO_3. La_2NiO_4 is formed in the absence of a flux, but if $La(NO_3)_3$ and $Ni(NO_3)_2$ are heated together at temperatures between 500 and 800 °C, a new phase is formed together with some nickel oxide impurity. We have not been able to identify this phase or to obtain it free from NiO. The X-ray pattern is given in Table 9, and does not resemble either $LaNiO_3$ or La_2NiO_4. Qualitative tests show that at least some of the nickel is in an oxidation state greater than II.

TABLE 8

X-Ray powder pattern of $YNiO_3$

$h\ k\ l$	d_{obs}	d_{cal}	I_{obs}	$h\ k\ l$	d_{obs}	d_{cal}	I_{obs}
1 0 0	5·18	5·18	10	3 0 1	1·676	1·681	15
0 0 2	3·72	3·72	40	1 1 4		1·670	
1 1 1	3·38	3·37	45	3 1 0	1·647	1·648	10
0 2 0	2·76	2·77	85	3 1 1	1·607	1·609	20
1 1 2	2·65	2·65	100	1 3 2	1·578	1·576	70
2 0 0	2·58	2·59	90	0 2 4	1·546	1·545	95
0 0 3	2·48	2·48	10	2 0 4	1·510	1·511	10
1 2 0	2·44	2·44	30	3 1 2		1·507	
2 1 0	2·355	2·345	25	0 3 3	1·476	1·481	15
1 2 1	2·319	2·320	40	2 3 1		1·473	
0 1 3	2·269	2·265	10	0 1 5	1·437	1·438	
1 0 3	2·238	2·238		3 2 1		1·437	25
2 1 1		2·237	45	1 0 5	1·433	1·431	
0 2 2	2·219	2·222		3 0 3	1·417	1·417	10
2 0 2	2·124	2·125	25	1 1 5	1·385	1·386	20
1 1 3	2·074	2·075	10	0 4 0		1·385	
2 1 2	1·989	1·984	5	3 1 3	1·371	1·373	20
2 2 0	1·894	1·891	80	2 2 4	1·328	1·327	30
0 0 4	1·859	1·861	55	4 0 0	1·295	1·294	55
2 2 1	1·834	1·833	25	2 3 3	1·286	1·286	10
2 0 3	1·791	1·792	10	4 0 1	1·275	1·275	15
0 3 1		1·791		1 3 4	1·270	1·271	20
1 2 3	1·741	1·741	20	3 3 0	1·261	1·261	5
1 3 0		1·739		0 0 6	1·241	1·241	40
2 1 3	1·702	1·705		3 1 4	1·233	1·234	30
1 3 1	1·690	1·694	35	2 4 0	1·221	1·221	5
2 2 2		1·684		2 4 1	1·205	1·205	25

Thus these compounds do not help in identifying the oxidation state of nickel in $BaNiO_3$. Unfortunately no physical technique exists which will yield the oxidation state directly.

(c) *Nickel*(IV) *Compounds*.—$SrNiO_3$ is best prepared by heating an equimolar mixture of $Sr(OH)_2 \cdot 8H_2O$ and NiO at 600 °C for 24 h under oxygen at 400 atm. $BaNiO_3$ may be prepared similarly: it may also be prepared by heating $BaNiO_2$ in a stream of oxygen at temperatures between 500 and 600 °C for *ca.* 30 h. It is strange that $BaNiO_{2\cdot5}$ cannot be converted into $BaNiO_3$ either under oxygen pressure or in a stream of oxygen at any temperature since it will be seen that the two compounds are isostructural and there is a continuous range of compositions between them.

TABLE 9

X-Ray powder pattern of an unidentified phase in the La–Ni–O system

d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}
3·77	25	2·73	45	1·998	5
3·48	10	2·71	40	1·918	40
2·78	100	2·149	20	1·675	5

$SrNiO_3$ and $BaNiO_3$ have similar *X*-ray powder patterns which were indexed in hexagonal symmetry. $BaNiO_3$ and $BaNiO_{2\cdot5}$ have the same structure. The structure consists of hexagonal stacking of $Sr(Ba)O_3$ layers with an ACAC sequence. The nickel(IV) ions lie at the centres of face-sharing octahedra. $SrNiO_3$ is one of the few strontium compounds which has a hexagonal close-packed structure. In this case at least, the size of A is not the determining factor for the stacking sequence of AO_3 layers.

Analytical data for the two compounds are consistent with their formulations. The mean oxidation state determined analytically is close to IV and in the case of the preparation from $BaNiO_2$ is confirmed by the gain in weight of the sample. It seems reasonable to exclude the possibility of mixtures of $Ni^{V} + Ni^{III}$ or $Ni^{VI} + Ni^{II}$ since these higher oxidation states are unknown. Moreover, both compounds are diamagnetic exactly as expected for a low-spin d^6 configuration.

Both $SrNiO_3$ and $BaNiO_3$ decompose in a stream of oxygen or air above 600 °C. Results of thermogravimetric studies of the formation and subsequent decomposition of $BaNiO_3$ are summarised in Table 10. In each case, the sample was heated slowly (0·5 to 1 °C min^{-1}) and then the desired temperature was kept constant until there was no further weight loss. Equilibrium was approached slowly and up to 12 h elapsed before weight losses ceased.

TABLE 10

Summary of t.g.a. studies of the reaction of $BaNiO_2$ with oxygen

t/°C	Composition on heating	Composition on cooling
20	$BaNiO_2$	$BaNiO_{2\cdot68}$
500	$BaNiO_{2\cdot98}$	$BaNiO_{2\cdot68}$
600	$BaNiO_{2\cdot98}$	$BaNiO_{2\cdot62}$
700	$BaNiO_{2\cdot92}$	$BaNiO_{2\cdot55}$
800	$BaNiO_{2\cdot62}$	$BaNiO_{2\cdot51}$
870	$BaNiO_{2\cdot57}$	$BaNiO_{2\cdot46}$
900	$BaNiO_{2\cdot45}$	

The maximum weight gain at 600 °C gave a composition close to $BaNiO_3$ but above 600 °C there is a stepwise loss of oxygen giving equilibrium compositions as low as $BaNiO_{2\cdot5}$ at 900 °C. When the temperature cycle is reversed there is some weight gain, but the maximum composition reached was $BaNiO_{2\cdot6}$, tending to confirm statements above that $BaNiO_{2\cdot5}$ cannot be converted into $BaNiO_3$ by heating in oxygen.

In order to study some of the intermediate compositions a furnace was arranged so that samples could be held at a desired temperature in a stream of oxygen and then rapidly quenched in liquid nitrogen. Five compositions were stabilised in this way: their analyses are in Table 2. There is good agreement between analytically determined oxidation states of these compounds and those deduced from weight changes in the t.g.a. study. The *X*-ray powder patterns of all five samples are similar to that of $BaNiO_{2\cdot5}$. The unit cell becomes progressively smaller as the composition approaches $BaNiO_3$. The changes are not linear and may be due to a combination of decrease in radius of the nickel ions as their oxidation state increases together with some shrinkage of the lattice as its oxygen-deficiency increases. In a similar way, $SrNiO_{2\cdot59}$ and $SrNiO_{2\cdot90}$ were made from $SrNiO_3$ at 650 and 430 °C, respectively, in oxygen.

The magnetic properties of the phases $BaNiO_x$, $x = 2{\cdot}57, 2{\cdot}69, 2{\cdot}79, 2{\cdot}85$, and 2·92, are listed in Tables 3 and 4, together with those of the two strontium compounds. In all cases, it was assumed that the nickel was present as nickel-(III) and -(IV) only and that any nickel(IV) would be diamagnetic. The quoted susceptibilities are thus appropriate to one gram atom of nickel(III). The values of μ_{eff} are reasonable for low-spin d^7 systems [*cf.* $Y(La)NiO_3$]. All obey Curie–Weiss laws, the θ values decreasing markedly as the proportion of nickel(III) decreases, as would be expected if the nickel(IV) is diamagnetic. There is some suggestion that interactions are greater in the strontium compounds than in those of barium as may be expected since the unit cells are smaller. Thus there is a continuous series of compositions at least in the range $BaNiO_{2\cdot5}$ to $BaNiO_3$, all having the same structure but with varying degrees of oxygen deficiency. The small θ values except for high concentrations of nickel(III) suggest that there is a random distribution of these ions in the lattice.

EXPERIMENTAL

Analyses.—With the exception of Al_2NiO_4 and $GaNiO_4$ which were analysed by neutron-activation methods, compounds were dissolved in hydrochloric acid and analysed as follows. Nickel was determined gravimetrically as the bisdimethylglyoximate, the filtrate being used for determination of the second metal (Sr, Ba, Y, or La). Strontium and barium were determined by titration with EDTA at pH = 12 using Methyl Thymol Blue as indicator. Barium is better determined by back titration of the excess of EDTA with standard strontium solution. In a few cases, barium was determined gravimetrically as the sulphate.

Yttrium and lanthanum were determined by back titration of the excess of EDTA with a standard zinc solution at pH = 4·6 using Xylenol Orange indicator.

The mean oxidation state of the nickel was determined by dissolving a known amount of the compound in acidified potassium iodide and titrating the liberated iodine with standard sodium thiosulphate. Blank determinations never exceeded two drops of titrant.

Neutron-activation analyses were performed by the staff of the Universities' Research Reactor, Risley.

X-Ray powder-diffraction patterns were obtained from a Phillips recording diffractometer using copper K_α radiation. An internal calibrant (quartz or potassium chloride) was added in each case.

Magnetic susceptibilities were measured by the Gouy method using conventional apparatus. The calibrant used was nickel chloride solution. Weiss constants were determined using the $\chi = c/(T + \theta)$ form of the Curie–Weiss law. All values of magnetic moments were calculated using the expression $\mu_{eff} = 2{\cdot}828(\chi_A . T)^{\frac{1}{2}}$.

Thermogravimetric data were obtained using a Stanton-Redcroft MF-H5 thermobalance, and diffuse reflectance spectra with a Beckman DK2A spectrometer, the reference reflector being magnesium oxide.

We thank the Iranian National Oil Company for financial support (to M. A.), the S.R.C. for a grant to purchase the thermobalance, and Professor W. S. Mackenzie of the Geology Department of Manchester University for the use of *X*-ray- and high pressure-facilities.

[4/1672 *Received, 5th August*, 1974]