

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY]

X-Ray Studies of the System Nickel-Oxygen-Water. I. Nickelous Oxide and Hydroxide¹

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Introduction

Numerous investigators² have made x-ray studies of natural and artificial nickelous oxide. The crystal structure has been definitely established as face centered cubic, with a lattice spacing approximately 4.17 Å. The most accurate determinations are probably those of Brentano³ (4.1705 Å.) and Ksanda⁴ (4.171 ± 0.003 Å.). Since both determinations were made with the use of sodium chloride diffraction as a primary standard, there is little doubt as to their accuracy.

There appear in the literature several reports of ostensibly new modifications of NiO. Lachand and Lepierre⁵ reported that the oxides prepared by ignition of what they believed to be two crystalline modifications of anhydrous nickel sulfate retained the external crystal form of the sulfates. The densities of the two oxides which they prepared were 6.67 g. per cc. and 6.70 g. per cc., as compared with a density of 6.80 g. per cc. calculated from x-ray data.

Hedvall⁶ found that NiO which had been repeatedly heated to 1000° for several hours in molten potassium chloride possessed a density of 7.45 g. per cc. Since this value is considerably higher than the density calculated from x-ray data of the normal form, it would appear that a new modification was present, and it has been treated as such in at least one instance.⁷

Prasad and Tendulkar⁸ have investigated the variation in physical properties, as influenced by temperature of preparation, of samples of NiO prepared by heating nickel nitrate, hydroxide and basic carbonate at temperatures of 400 to 1000°. The oxide obtained at 400° was black and the one at 1000° green. They found that the density and electrical resistance increased, and the rate of solution in sulfuric acid decreased as the temperature of preparation was raised. They concluded that there were two forms of NiO, the black form prepared at 400° and the greenish-gray form, at 1000°. The changes in properties were attributed to changes

(1) From a thesis submitted by Robert W. Cairns in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Davey and Hoffman, *Phys. Rev.*, **15**, 333 (1920); Davey, *ibid.*, **17**, 402 (1921); Clark, Asbury and Wick, *THIS JOURNAL*, **47**, 2661 (1925); Lunde, *Z. anorg. allgem. Chem.*, **163**, 345 (1927); Hendricks, Jefferson and Schultz, *Z. Kryst.*, **73**, 376 (1930).

(3) Brentano, *Proc. Roy. Soc. (London)*, **37**, 184 (1925); *Phil. Mag.*, [7] **3**, 413 (1927).

(4) Ksanda, *Am. J. Sci.*, **22**, 131 (1931).

(5) Lachand and Lepierre, *Bull. soc. chim.*, [3] **7**, 600 (1892).

(6) Hedvall, *Z. anorg. allgem. Chem.*, **92**, 382 (1915).

(7) See Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5 Auflage, I, p. 304 (1923).

(8) Prasad and Tendulkar, *J. Chem. Soc.*, 1403 (1931).

(1) in particle size, (2) from amorphous to crystalline state, (3) in crystalline form and (4) of an intramolecular nature.

Leblanc and Sachse⁹ have shown that the oxide prepared by the same method at 400 to 500° possessed the normal cubic structure of the high-temperature preparation as evidenced by the x-ray diffraction pattern. They have also proved that the black color was due to traces of active oxygen.

Further, a new modification of nickel oxide was reported by Bennett, Cairns and Ott¹⁰ but further work has shown that the reported results were erroneous. The substance then reported as NiO by Dr. Bennett¹¹ was subsequently found by us to contain active oxygen and water in bound form. That the diffraction pattern appeared in the first approximation to fit a cubic structure, was purely accidental. A search of the literature revealed no other reports of different modifications of nickelous oxide.

Inasmuch as there has been no x-ray evidence to disprove or substantiate the existence of the different modifications as reported, the present investigation was undertaken. Incidental to this work more accurate data were obtained on the crystal structure of nickelous hydroxide. The crystal structure of nickelous hydroxide has previously been determined by Natta.¹² The lattice type was found to be hexagonal with one molecule per unit cell. The lattice constants as determined by the x-ray diffraction were $a_0 = 3.07 \text{ \AA}$. and $c_0 = 4.61 \text{ \AA}$.

Nickelous hydroxide as generally prepared by precipitation from nickel salt solutions contains, after drying, more water than is necessary for a composition of $\text{Ni}(\text{OH})_2$. In some cases this has been taken as evidence of the formation of definite hydrates.¹³

Experimental Part

Preparation of Samples

Nickel Oxides from Sulfates.—Twenty grams of ammonium bisulfate and ten grams of nickel sulfate hexahydrate were fused together in a porcelain crucible. The bisulfate was volatilized by heating the mass to red heat for four hours. The residue of crystalline anhydrous nickel sulfate was found by microscopic examination to be in the form of yellow-green transparent octahedra. In a second preparation, the same procedure was followed except that 3 g. of concd. sulfuric acid was added to the mixed sulfates before fusion. The sulfate product in this case crystallized in lens-shaped crystals. x-Ray powder pictures of the two sulfates were identical, and their complexity indicated low symmetry for the crystal structure. Thus the two forms of nickelous sulfate do not represent two different modifications, but are merely different habits.

Each of the two preparations of nickel sulfate was heated at white heat in a platinum crucible for an hour. The oxide products were moss-green in color and retained the external form of the original sulfates.

Pure Nickelous Oxide from the Nitrate.—C. P. nickel nitrate was twice recrystal-

(9) Leblanc and Sachse, *Z. Elektrochem.*, **32**, 204 (1926).

(10) Bennett, Cairns and Ott, *THIS JOURNAL*, **63**, 1179 (1931).

(11) Bennett, Dissertation, Johns Hopkins University, 1930.

(12) Natta, *Gazz. chim. ital.*, **58**, 344 (1928).

(13) See Gmelin-Kraut, "Handbuch der anorg. Chem." Vol. 1, pp. 43-44 (1909).

ized from water. The nitrate initially gave a very faint test for cobalt by Vogel's method, but this was negative after one recrystallization. The purified nitrate was heated to white heat in a platinum crucible. A surface layer of dark colored oxide was formed due to contact with air, but beneath this the pure NiO was yellow-green and gave no test for active oxygen by the Bunsen method.

The purified nitrate was also treated in solution with ammonia gas, and the precipitated hexammoniate was further recrystallized twice from strong ammonia solution. The product was ignited in nitrogen in an electric furnace at 1000° . The oxide thus formed was also green and contained no active oxygen.

Nickelous Oxide by Hedvall's Method.—Pure NiO was heated in molten potassium chloride at white heat over a period of five hours. The heating was momentarily interrupted every half hour and the mass allowed to cool for five minutes. At the conclusion of the heating the potassium chloride was leached out with water and the light green oxide filtered off and washed.

Nickelous Oxide by Decomposition of Nickelic Oxide Hydrate.—A sample of nickelic oxide-hydrate, the approximate composition of which was $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (see following paper), was heated for three days at 120° . The black color remained although only a trace of active oxygen was present. The same oxide-hydrate was heated in nitrogen at 1000° for two hours. The green product thus formed contained no active oxygen.

Nickelous Hydroxide.—A solution of 25 g. of potassium hydroxide in 250 cc. of water was added dropwise to a solution of 60 g. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 500 cc. of water at room temperature. The precipitation was carried out with rapid stirring in a closed three-necked flask of three liters capacity. Carbon dioxide-free air was kept over the solution. After precipitation the product was washed by decantation three times, in a cylinder of ten liters capacity. The cylinder was kept covered with a ground-glass plate except during decantation. A minimum time of exposure to air was allowed, and carbon dioxide-free water was used in the decantation. After the supernatant liquid had been removed in the last decantation, the precipitate was filtered with suction on a covered Buchner filter. After washing, the product was dried in a desiccator for two weeks over concd. sulfuric acid.

The preparation was repeated with the nitrate solution kept at 100° during precipitation. The final composition of this product, after drying *in vacuo* over calcium chloride for a day, was $\text{NiO} \cdot 1.21\text{H}_2\text{O}$, as shown by nickel and water analyses. The product contained 0.6% of carbon dioxide. Another preparation was carried out at 0° , and the product was kept in the wet state for x-ray investigation.

Method of x-Ray Analyses.—The source of x-rays was a hot filament metal tube with a copper anticathode (model Dr. Seeman, Freiburg). The tube was operated at *ca.* 20 kilovolts and 30–40 milliamperes. Nickel foil was used for practically complete absorption of K_{β} -radiation. The radiation was occasionally checked spectroscopically and found to be CuK_{α} essentially. The camera was of the Debye-Scherrer type (Dr. Leiss, Berlin-Steglitz) with an effective diameter of 114.6 mm. The powdered samples were contained in thin collodion tubes of 0.5 mm. diameter. In the accurate determinations the samples were powdered in an agate mortar with equal parts of Kahlbaum "sodium chloride for analysis." The diffraction of sodium chloride thus appeared on the films and was used as a standard in measurement of the diffraction of the nickel compounds. The values of $\sin \theta$ for the glancing angles for sodium chloride were first determined from microcomparator measurements of the line spacings on the films and the known diameter of the camera. These values were then compared with the values calculated assuming $a_0 = 5.628 \text{ \AA.}$ for chemically pure sodium chloride. A plot of these corrections against the values of $\sin \theta$, uncorrected, was used to determine the corrections to the observed sines of the glancing angles for NiO and $\text{Ni}(\text{OH})_2$.

Some of the diagrams obtained may be found in a following paper.

Results of x-Ray Analysis

Nickelous Oxide.—The two samples of nickel oxide prepared by ignition of the sulfates gave x-ray diffractions corresponding to the usual face-centered type of crystal. There was no distortion of the lattice within the limits of experimental error. It was evident that the oxides were merely pseudomorphic with the original sulfates.

TABLE I
NiO FROM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Compound	Miller indices	Sin θ obs.	Sin θ corr.	a_0 for NiO, Å.
NaCl	200	0.27626	0.27363
NiO	111	.32227	.31992	4.1688
NiO	200	.37156	.36956	4.1671
NaCl	220	.38873	.38697
NaCl	222	.47533	.47393
NiO	220	.52362	.52258	4.1674
NaCl	400	.54801	.54726
NiO	311	.61291	.61242	4.1699
NiO	222	.64026	.63994	4.1681
NaCl	422	.67075	.67025
NiO	400	.73875	.73905	4.1675
NaCl	440	.77375	.77393
NiO	331	.80412	.80482	4.1702
NaCl	442	.81991	.82089
NiO	420	.82511	.82595	4.1691
NaCl	620	.86410	.86530
Average value for a_0 for NiO				= 4.1685
Average deviation from the mean for a_0				= 0.0008

TABLE II
NiO FROM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$

Compound	Miller indices	Sin θ obs.	Sin θ corr.	a_0 for NiO, Å.
NaCl	200	0.27607	0.27363
NiO	111	.32207	.32100	4.1677
NiO	200	.37118	.36947	4.1681
NaCl	220	.38854	.38697
NaCl	222	.47486	.47393
NiO	220	.52324	.52269	4.1666
NaCl	400	.54756	.54726
NiO	311	.61257	.61249	4.1695
NiO	222	.63978	.63983	4.1688
NaCl	422	.67043	.67025
NiO	400	.73846	.73896	4.1680
NaCl	440	.77329	.77393
NiO	331	.80412	.80490	4.1699
NaCl	442	.82015	.82089
NiO	420	.82536	.82616	4.1681
NaCl	620	.86427	.86530
Average value for a_0 for NiO				= 4.1683
Average deviation from the mean for a_0				= 0.0008

Data on the x-ray diffractions of the two samples prepared from nickel nitrate hexahydrate and hexammoniate are given in Table I and Table II.

The average of these two determinations was then 4.1684 Å. In consideration of the accuracy possible through use of sodium chloride as a primary standard and, because of the purity of the samples, this value is probably accurate to 0.001 Å.

By an identical determination the nickelous oxide prepared by Hedvall's method was found to have the lattice constant, $a_0 = 4.1665$ Å. The average deviation from the mean value for a_0 was in this case 0.0007 Å. Thus this value is identical with the above ones within the experimental error (± 0.001). Hence it appears that Hedvall's density determination was subject to error, as an experimental density of 7.45 g. per cc. would require a lattice spacing of 4.04 Å. or less.

The two samples of nickelous oxide prepared by decomposition of nickelic oxide hydrate at 120 and 1000° possessed identical crystal diffraction, with the exception that the diffraction lines of the low temperature preparation were exceedingly diffuse, while those of the sample ignited at 1000° were very sharp. The differences in properties observed by Prasad and Tendulkar⁸ could all be explained on the basis of a difference in particle size. The black color was caused by traces of active oxygen.

TABLE III
Ni(OH)₂ PRECIPITATED AT 100°

<i>hkl</i>	Sin θ obs.	Sin θ corr.	Sin θ corr.	Sin θ calcd.
001	0.17021	0.16676	0.02781	0.02794
100	.28736	.28501	.08123	.08152
{ 101 }	.33258	.33065	.10933	{ .10946 }
{ 002 }				{ .11176 }
102	.44072	.43980	.19342	.19329
{ 110 }	.49470	.49428	.24431	{ .24457 }
{ 003 }				{ .25147 }
111	.52139	.52121	.27166	.27251
200	.57071	.57100	.32604	.32610
103	.57715	.57749	.33349	.33299
{ 201 }	.59377	.59428	.35357	{ .35404 }
{ 112 }				{ .35634 }
{ 202 }	.66066	.66178	.43795	{ .43783 }
{ 004 }				{ .44706 }

$$a_0 = 3.114 \text{ \AA.}; c_0 = 4.617 \text{ \AA.}; c/a = 1.483$$

NaCl Diffraction

<i>hkl</i>	Sin θ obs.	Sin θ calcd.
200	0.27620	0.27363
220	.38832	.38697
222	.47460	.47393
400	.54683	.54726
420	.61130	.61185
422	.66913	.67025

Nickelous Hydroxide.—The room temperature preparation gave a very diffuse x-ray diffraction pattern with the innermost line (corresponding to the (001) spacing)¹⁴ a very broad band. The preparation made at 100° gave much sharper diffraction lines and all of the inner lines were clear enough for accurate measurement with a millimeter rule. The diffraction pattern corresponded to that of a crystal of hexagonal lattice type. Data are given in Table III.

The average deviation between the values of $\sin^2 \theta$ observed and $\sin^2 \theta$ calculated from the quadratic formula for the hexagonal system was 0.18%, with the values of the lattice constants $a_0 = 3.114 \text{ \AA.}$ and $c_0 = 4.617 \text{ \AA.}$ A second determination gave agreement to 0.28%. Our more accurate value for a_0 differs by *ca.* 1% from Natta's.¹²

The calculated density was 3.94 g. per cc. for one molecule per unit cell, in fair agreement with a determined density of 3.56 g. per cc., the discrepancy being due probably to adhering air and water.

Expressed on rhombohedral axes the unit cell contained three molecules per unit cell, showing that the hexagonal type was the simplest structure.

In a previous determination¹² the structure was assumed to be of the cadmium iodide type, with the atoms of Ni(OH)_2 at the following positions of D_{3d}^3 : Ni at 0, 0, 0; OH at $1/3, 2/3, u$; $2/3, 1/2, \bar{u}$. The optimum value of u was found to be 0.25.

In this work the atomic positions were assumed to be the above, and the relative intensities of the planar reflections were computed from the formula

$$I \propto \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot j \cdot \left(F_{\text{Ni}} + F_{\text{O}} \cos 2\pi \left(\frac{h+2k}{3} + ul \right) \right)^2$$

where j is the heaping factor¹⁵ for the plane ($h k l$) and F_{Ni} and F_{O} are the atomic reflecting powers for Ni and O atoms.¹⁶

TABLE IV

Ni(OH)₂

$h k l$	Observed intensity	$u = 0.23$	Calculated intensity	
			0.25	0.27
001	Very strong	93	79	65
100	Medium strong	25	25	25
101	Very strong	50	49	47
102	Medium strong	18	23	28
110	Medium strong	22	23	25
111	Medium weak	8	7	6
200	Very weak	5	5	5
103	Very weak	5.5	5	5
201	Medium weak	7	7	7
202	Medium weak	6	5.5	4.5

(14) It is of interest to note that this important spacing was not directly observed in the previous work of Natta.

(15) Schleede and Schneider, "Röntgenspektroskopie und Kristallstrukturanalyse." Band II, p. 250, Table 33, Berlin, 1929.

(16) Wyckoff, *Phys. Rev.*, **35**, 583 (1930).

The intensities, in arbitrary units, for different values of the parameter u are given in Table IV. The best agreement with observed intensities was found for $u = 0.25$, confirming Natta's results.

The x-ray diffraction of a wet, freshly precipitated sample of $\text{Ni}(\text{OH})_2$ prepared at 0° showed a very diffuse diffraction in which all the lines corresponded to the strongest reflections of the dry material. No evidence could be found of any definite hydrates of $\text{Ni}(\text{OH})_2$.

A sample of NiO , obtained by decomposition of $\text{Ni}(\text{OH})_2$ in nitrogen at 500° , showed no change in its x-ray diffraction after the material had been heated in a bomb tube in water at 150° for five days. Hüttig and Peter¹⁷ have found that nickelous hydroxide cannot be formed by action of water at room temperature on NiO . Thus it appears that the decomposition of nickelous hydroxide to the oxide is not reversible under ordinary pressures.

Summary

1. It has been found that several new modifications of nickelous oxide reported in the literature conform to the usual face-centered type of lattice. The lattice constant for preparations made according to the methods described did not vary from the accepted value for the normal form of the oxide, within the limits of experimental error.

2. The lattice constant of pure NiO has been redetermined more accurately using pure sodium chloride as a reference substance. The value as determined for two different preparations of nickelous oxide was

$$a_0 = 4.1684 \pm 0.001 \text{ \AA.}$$

3. It has been possible to redetermine the lattice constants of hexagonal $\text{Ni}(\text{OH})_2$ with greater accuracy than heretofore. The lattice constants were found to be $a_0 = 3.114 \pm 0.005 \text{ \AA.}$ and $c_0 = 4.167 \pm 0.005 \text{ \AA.}$ Intensity calculations indicated that the crystal had the symmetry of the space group D_{3d}^3 , with the following atomic coördinates: Ni at $(0, 0, 0)$; OH at $(\frac{1}{3}, \frac{2}{3}, 0.25)$, $(\frac{2}{3}, \frac{1}{3}, -0.25)$, in accordance with a previously reported structure determination.

4. The reported existence of hydrates of $\text{Ni}(\text{OH})_2$ has been disproved.

5. Two crystal forms of nickel sulfate, previously thought to be different modifications, were found to be identical, differing only in crystalline habit. The nickel oxides prepared from the sulfates were merely pseudomorphic with them, and do not represent new modifications.

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(17) Hüttig and Peter, *Z. anorg. allgem. Chem.*, **189**, 184 (1930).