348. *Structural Modifications of* β-NiO·OH.

By G. W. D. Briggs.

The existence of additional reflections in the X-ray diffraction pattern of β-NiO·OH is reported, and a modified form of the oxide obtained by electrodeposition in the presence of foreign ions is described.

The higher nickel oxides of composition near Ni_2O_3,xH_2O or NiO·OH were first described [1] in detail by Glemser and Einerhand in 1950. These authors distinguished three forms of NiOOH, designated α, β, and γ, of which β-NiO·OH was obtained by precipitation or by anodic deposition from an acetate-buffered nickel sulphate solution at room temperature. They obtained an X-ray powder pattern from the β-form showing three diffuse lines at 4·9, 2·42, and 1·4 Å, and regarded these as the 001, 100, and 110 reflexions from a hexagonal lattice derived from that of $Ni(OH)_2$. Whilst examining the electrolytically formed oxide in these laboratories we observed some additional features of the X-ray diffraction pattern and have also distinguished a modified form of the oxide.

Examples of the diffraction patterns obtained are shown in the Plate. They were taken with Ni-filtered Cu-$K\alpha$ radiation and a 6 cm. cylindrical camera, the oxide being contained in a glass capillary of 0·3 mm. bore. Plate *a* shows the diffraction pattern obtained from oxide of composition $Ni_2O_{3\cdot04},2\cdot6H_2O$ deposited on nickel from a 0·5N-solution of nickel nitrate made N in sodium acetate, at a constant current of about 10 mA/cm.^{2}. It has strong lines at 4·8, 2·44, and 1·41 Å, corresponding to those listed by Glemser and Einerhand; but it shows also a strong line at 9·5 Å, a weak line at 3·2 Å, and indications of a very weak reflection at about 1·2 Å, none of these being mentioned by Glemser and Einerhand. The 2·4 Å line is also unsymmetrical in shape, as shown by the photometer trace, Fig. *a*. It may, therefore, be a two-dimensional (*hk*) reflection from a random layer lattice,[2] although the appearance could also be due to the presence of another broad band near 2·0 Å.

If the oxide is deposited in a solution buffered with potassium instead of sodium acetate, or if potassium nitrate is simply added to the bath at a concentration of about N, the modified diffraction pattern shown in Plate *b* and Fig. *b* is obtained. This has a strong inner line as before, but the spacing is about 7·6 Å as compared with 9·5 Å for the normal preparation. The strong line at 4·8 Å is replaced by a very broad diffuse band usually showing indistinct peaks at about 4·8 and 3·5 Å, the remaining lines appearing as in the normal pattern (Plate *a*).

These results suggested experiments with the addition of other ions to the depositing solution and it was found that the normal pattern (Plate *a*) was obtained in the presence of Li^+, Ca^{2+}, and Sr^{2+}, whereas the modified pattern (Plate *b*) was obtained with K^+, Ba^{2+}, Cs^+. As similar conditions were used for the deposition of each oxide, it seemed unlikely that electrochemical factors could be directly responsible for the change in structure, and the oxides were therefore examined for possible retention of foreign ions. The material was deposited on a large nickel anode, washed by suspension in water, and rapidly dried *in vacuo*, the effectiveness of washing being judged by the amount of sodium retained by the samples. Nickel, barium, and strontium were estimated by standard gravimetric methods; active oxygen iodometrically; sodium, potassium, and calcium by flame photometer; and water contents were obtained by difference.

The results tabulated show that, whereas sodium could be removed fairly easily from the oxides by adequate washing, potassium, calcium, strontium, and barium appeared to be strongly retained, the proportion of barium being much the largest and amounting to about 1 Ba per 12 Ni atoms. Although calcium and strontium seemed to be retained in

---

[1] Glemser and Einerhand, *Z. anorg. Chem.*, 1950, **261**, 26, 42.

[2] Warren, *Phys. Rev.*, 1941, **59**, 693; Brindley, "X-Ray Structure and Identification of Clay Minerals," Mineralogical Society (Clay Minerals Group), London, 1951, p. 285.

FIGURE. *Photometer traces corresponding to specimens a and b.*

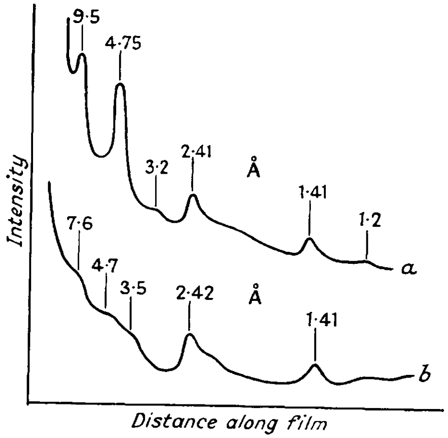
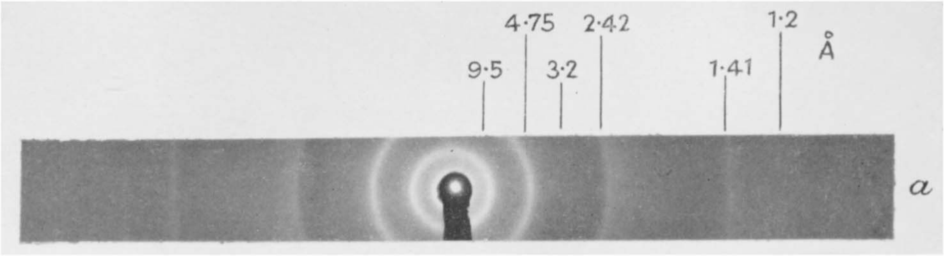
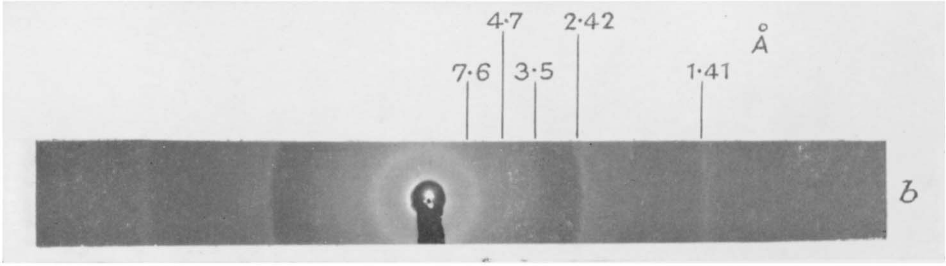


PLATE. *Diffraction patterns of electrolytically deposited nickel oxides.*





[*To face p.* 1816.

amounts comparable with those for potassium, the resulting oxides gave the normal diffraction pattern. This evidence suggests that the modified β-NiO·OH structure may be due to the retention by the oxide of relatively large ions. The possibility of a related change in the water content of the oxide, which considerably exceeds that required by the formula NiO·OH or Ni_2O_3,H_2O, is not excluded by our present evidence.

Solution used for deposition	Diff. pattern of oxide	Alkali-metal retained (%)	Compn. of oxide
0·5N-$Ni(NO_3)_2$ + N-NaOAc	Plate *a*	0·06	$Na_{0\cdot005}Ni_2O_{3\cdot03},2\cdot6H_2O$
,, + N-$Ca(NO_3)_2$	,,	1·5	$Ca_{0\cdot08}Ni_2O_{3\cdot01},2\cdot8H_2O$
,, + N-$Sr(NO_3)_2$	,,	1·5	—
,, + N-KNO_3	Plate *b*	1·23	$K_{0\cdot06}Ni_2O_{2\cdot94},2\cdot7H_2O$
,, + satd. $Ba(NO_3)_2$	,,	9·3	$Ba_{0\cdot17}Ni_2O_{3\cdot17},3\cdot3H_2O$

The additional lines observed in the *X*-ray diffraction pattern of β-NiO·OH may be accommodated by a slight modification to the indexing proposed by Glemser and Einerhand, since the spacings of 9·5, 4·8, 3·2, 2·4, 1·4, and 1·2 Å would correspond to the 001, 002, 003, 100, 110, and 200 reflections respectively from a hexagonal lattice with unit cell $a = 2\cdot8$ Å and $c = 9\cdot5$ Å. Although an adjustment of this kind is feasible, we feel that our results show the need for a fuller investigation of these oxides before a detailed account of their structure is attempted. For example, the existence of mixed layer lattices analogous to those formed by some groups of clay minerals, may be implied by the large and variable water contents of the oxides and by the changes in apparently prominent basal spacings brought about in the presence of large foreign ions.

The author thanks Professor W. F. K. Wynne-Jones for providing facilities and encouragement, Dr. H. P. Stadler for most helpful discussion of the *X*-ray results, Mr. J. Shaw for analyses of sodium, potassium, and calcium, and the Electricity Supply Research Council of the Central Electricity Authority for their support of this work.

King's College, University of Durham,
Newcastle upon Tyne, 1.

[*Received, December 5th,* 1956.]