Acta Cryst. (1948). **1**, 226

A note on the structure of nickel oxide at subnormal and elevated temperatures.*

By H. P. Rooksby.
Research Laboratories of The General Electric Company, Wembley, England

(*Received* 23 *June* 1948)

Introduction

In a previous communication (Rooksby, 1943) it was reported that critical examination of X-ray powder photographs of nickel oxide disclosed a departure of the crystal structure from cubic symmetry. Certain of the X-ray powder lines show multiplicity that can be explained if it is assumed that the structure is deformed by a small contraction along one of the triad axes. A rhombohedral cell with axial angle 60° 4·2′ then represents the true crystal structure.

It was concluded that the atomic size ratio of nickel to oxygen is just too small at room temperature for a face-centred cubic structure to be maintained. In accord with this conclusion it might be expected that the departure from cubic symmetry would become greater at low temperatures but would disappear at some temperature above room temperature. It has been possible to show that these predictions are correct by taking X-ray powder photographs at liquid-air temperature and at temperatures between room temperature and 300° C.

Experimental results

The method of Lonsdale & Smith (1941) was employed for the liquid-air temperature examination. It was found convenient to register the back-reflexion 422 with Ni radiation, and Fig. 1 compares the appearance of this reflexion when the specimen was at room temperature and when liquid air was streaming over its surface. The film was held in a flat cassette at a distance of approximately 9 cm. from the specimen.

Owing to the rhombohedral deformation of the face-centred cubic structure, the 422 line is split into three components, though one of these is too weak to be readily distinguished. The separation of the strongest two components is decidedly the greater at liquid-air temperature, corresponding with an increase of the rhombohedral angle from 60° 4·2′ to 60° 12′.

High-temperature X-ray powder photographs were obtained with Co K radiation (unfiltered) in a 19 cm. diameter camera of the Owen (1943) type. Lines 331, 422(β), and 420 provided a sensitive guide to the extent of the rhombohedral deformation from the face-centred cubic structure. The 400 α-doublet proved useful as a means of checking that high resolution was maintained, as this line is not affected by the departure from cubic symmetry.

It was found that the rhombohedral distortion became progressively smaller as the temperature of the specimen was raised. Some distortion could still be detected at 150° C., but was not noticeable above 200° C. Fig. 2 compares the relevant sections of the X-ray patterns at room temperature, 105 and 275° C. respectively. The results are summarized in Table 1.

Table 1. *Summary of crystal structure data on* NiO

Temperature (° C.)	Symmetry	Lattice constants
−183	Rhombohedral	$a = 2{\cdot}946 \pm 0{\cdot}001$ A., $\alpha = 60°\ 12'$
18	Rhombohedral	$a = 2{\cdot}9518 + 0{\cdot}0005$ A., $\alpha = 60°\ 4{\cdot}2'$
275	Face-centred cubic	$a_0 = 4{\cdot}1946 \pm 0{\cdot}0005$ A. (Corresponding rhombohedral cell: $a = 2{\cdot}9660 \pm 0{\cdot}0004$ A., $\alpha = 60°$)

No abnormalities in the structural transition could be detected, the elimination of the rhombohedral distortion taking place smoothly with rise of temperature. The lattice parameter of the face-centred cubic structure at 275° C. is $4{\cdot}1946 \pm 0{\cdot}0005$ A. (on the basis

$$\lambda(\text{Co } K\alpha_1) = 1{\cdot}78890 \text{ A.}).$$

Discussion

The nickel oxide structure provides a simple example of distortion effects resulting from close-packing of ions of slightly unfavourable size ratio. If the structure is regarded as built up of close-packed layers of nickel and oxygen ions, stacked alternately in a [111] direction of the face-centred cubic lattice, the size ratio becomes unfavourable below a temperature of about 200° C. The resultant departure from cubic symmetry increases progressively with decrease of temperature.

In this connexion it is interesting to observe that solid solution of small percentages of monoxides of metals having a larger atomic radius than nickel, e.g. ferrous oxide or cobaltous oxide, enables cubic symmetry to be maintained at room temperature. No distortion is indicated in X-ray powder photographs of nickel oxide containing 5% by weight of ferrous oxide or 10% by weight of cobaltous oxide.

References

Lonsdale, K. & Smith, H. (1941). *J. Sci. Instrum.* **18**, 133.
Owen, E. A. (1943). *J. Sci. Instrum.* **20**, 190.
Rooksby, H. P. (1943). *Nature, Lond.*, **152**, 304.

* Communication no. 408 from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.

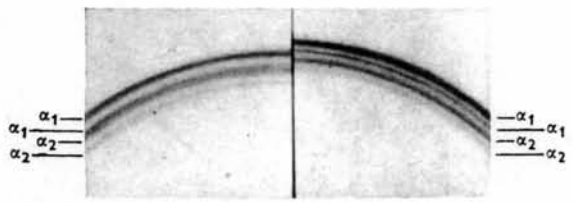

Fig. 1. Comparison between 422 (cubic) reflections of powdered nickel oxide. On left at −183° C.; on right at 18° C.

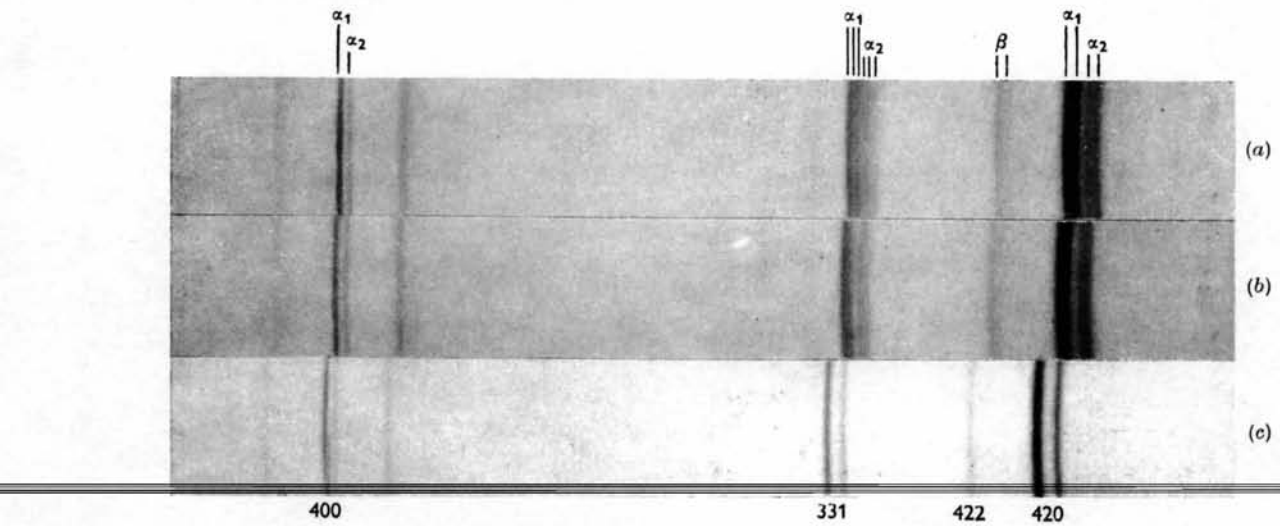

Fig. 2. Parts of X-ray powder photographs (Co K radiation; 19 cm. camera) of nickel oxide at temperatures: (*a*) 18° C.; (*b*) 105° C.; (*c*) 275° C.

[*To face p.* 226