

Short Communications

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The structure of cobalt oxide, Co_3O_4 . By W. L. SMITH and A. D. HOBSON, *Warren Spring Laboratory, P.O. Box 20, Stevenage, Herts. SG1 2BX, England*

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The powder diffraction pattern of Co_3O_4 has been re-examined and new values are given for the structural parameters. The results are consistent with data on related compounds, and show that the $\text{Co}^{2+}-\text{O}^{3-}$ distance in the low-spin compound Co_3O_4 differs only slightly from the corresponding distance in the high-spin compound LaCoO_3 .

Introduction

During a study of cobalt oxide catalysts it was found that the interionic distances in Co_3O_4 were not well established. This note reports a new determination of the structure from the X-ray powder-diffraction pattern.

Cossee (1956) showed from magnetic measurements that Co_3O_4 possesses the normal spinel structure $A[\text{B}_2]\text{O}_4$, with the Co^{2+} ions occupying the tetrahedral (or *A*) sites, and the Co^{3+} ions the octahedral (or *B*) sites. The interionic distances in the spinel lattice are determined by the cell constant *a* and the oxygen parameter *u*, which in the ideal structure takes the value 0.375 [for further details see Gorter (1954)]. Values of *u* can be determined from the relative intensities in the powder-diffraction pattern, especially from that of the 111 reflexion, which is weak when $u=0.375$ but which becomes stronger as *u* increases. The first determination of *u* in this way was apparently that of Verwey & de Boer (1936), who found $u=0.380 \pm 0.005$ from photometric measurements. These authors noted that such a value was difficult to reconcile with the structure $\text{Co}^{2+}[\text{Co}_2^{3+}]\text{O}_4$. A recent tabulation of crystallographic data (Pearson, 1967) quotes $u=0.3895$, but gives effectively no details. Renewed investigation of the diffraction pattern seemed desirable.

Cossee (1956) concluded that the cobaltic ions in Co_3O_4 are diamagnetic, or in the low-spin state, in contrast to the perovskite LaCoO_3 , where the cobaltic ions are known to be paramagnetic and in the high-spin state (Jonker & Van Santen, 1953). There are theoretical reasons for expecting the cobalt-oxygen distance in low-spin compounds to be less than in high-spin compounds (see, for example, Martin & White 1968), but earlier comparisons of the structures of Co_3O_4 and LaCoO_3 suggested the opposite (Goodenough, 1958). As shown below, the present analysis of the X-ray data for Co_3O_4 removes this anomaly.

Results

Samples of cobalt oxide were prepared by thermal decomposition of cobalt oxalate and nitrate, and diffraction patterns were recorded using $\text{Cu K}\alpha$ radiation and a Philips powder diffractometer. The fluorescent component of the scattered radiation was effectively eliminated by a focusing lithium fluoride crystal monochromator. The relative intensities of the 111, 311 and 222 reflexions were determined by

planimeter measurement of the areas beneath the diffraction profiles, and are given in Table 1.

Table 1. *Relative intensities in the Co_3O_4 diffraction pattern*

Reflexion	Intensity (relative to 311)	
	Observed (mean of 3 samples)	Calculated $u=0.392$
111	14	14.2
311	100	100
222	8	10.4

The relative intensities are determined by the multiplicity of the reflexions concerned, the appropriate Lorentz-polarization terms, and the squares of the structure factors. The Lorentz-polarization factor is more complex than usual owing to the monochromation of the diffracted beam (see *e.g.* Arndt & Willis, 1966) and is given by

$$L(\theta) = \frac{1 + k(\theta)_m \cos^2 2\theta}{(1 + \cos^2 2\theta) \sin^2 \theta \cos \theta} \quad (1)$$

where θ and θ_m are the Bragg angles of reflexion from the sample and monochromator respectively. $k(\theta_m)$ is the polarization factor for the monochromator, and is best determined experimentally (see Jennings, 1968); however, over the restricted range of 2θ appropriate to this work, the analysis of the relative intensities to give the *u* parameter is insensitive to the exact value chosen for *k* (which can lie between $\cos^2 2\theta_m$ and 1), and a detailed investigation of the polarization characteristics of the monochromator is not necessary. Experimental work has suggested that for the LiF monochromator used here, *k* is in fact satisfactorily approximated by the perfect crystal value $|\cos 2\theta_m|$, which has also been recommended by Witz (1969). For the 200 reflexion of LiF, $|\cos 2\theta_m|=0.707$, and *k* was given this value in the work reported here. The structure factors were calculated for various values of the anion parameter *u*, using the formulae and atomic scattering factor data given in *International Tables for X-ray Crystallography* (1952). In this way it was concluded that $u=0.392 \pm 0.002$. Calculated and observed intensities are compared in Table 1. This

value of u also gives a satisfactory representation of the intensities given by Swanson, Cook, Isaacs & Evans (1960), who used a diffractometer with cobalt $K\alpha$ radiation (presumably not monochromated).

Discussion

Interionic distances in Co_3O_4 may be calculated from u and the lattice constant a (see Gorter, 1954); if $u=0.392$ and $a=8.084 \text{ \AA}$ (Swanson *et al.*, 1960) it is found that (to about $\pm 0.02 \text{ \AA}$)

$$\begin{aligned}\text{Co}^{3+}-\text{O}^{2-} &= 1.89 \text{ \AA} \\ \text{Co}^{2+}-\text{O}^{2-} &= 1.99 \text{ \AA}.\end{aligned}$$

The cobaltite $\text{Zn}[\text{Co}_2\text{O}_4]$ has recently been re-examined by Rasines (1972) who gave X-ray intensity data measured on a diffractometer using Co $K\alpha$ radiation. Rasines does not give a value for the u parameter, but his data may be analysed to give $u=0.395$. This, together with Rasines' a value (8.088 \AA), leads to the distances:

$$\begin{aligned}\text{Co}^{3+}-\text{O}^{2-} &= 1.87 \text{ \AA} \\ \text{Zn}^{2+}-\text{O}^{2-} &= 2.03 \text{ \AA}.\end{aligned}$$

These distances differ considerably from previous estimates (see Goodenough, 1958), but when they are compared with the interionic distances in related compounds a consistent pattern emerges which lends encouraging support to the present conclusions. The $\text{Co}^{3+}-\text{O}^{2-}$ distance in LaCoO_3 (where the cobalt is octahedrally coordinated) is 1.91 \AA (Askham, Fankuchen & Ward, 1950). The octahedrally coordinated Co^{2+} ions in CoO are 2.13 \AA distant from the oxygen anions (Swanson *et al.*, 1960), but for comparison with the tetrahedrally coordinated Co^{2+} ions in Co_3O_4 this distance must be multiplied by ~ 0.94 giving a value of 2.00 \AA (see, *e.g.*, Pauling, 1960). In ZnO each zinc ion is surrounded by four oxygen anions, three of which are at a distance of 2.04 \AA (Wyckoff, 1963).

The $\text{Co}^{3+}-\text{O}^{2-}$ distances in the various oxides are compared in Table 2, which is based on that of Martin & White (1968), but which uses the data of this paper.

Table 2. Interionic distances in cobalt oxides

Compound	High spin %	Low spin %	$\text{Co}^{3+}-\text{O}^{2-}$ distance in \AA
ZnCo_2O_4	15.5	84.5	1.87
Co_3O_4	0	100	1.89
LaCoO_3	100	0	1.91*

* Askham *et al.* (1950).

The second and third columns give the percentage distribution of the cobaltic ions between high- and low-spin states (see references given by Goodenough, 1958). It is seen that the anomalous lengthening of the $\text{Co}^{3+}-\text{O}^{2-}$ distance in the high-spin states, which was remarked upon by Martin & White (1958), and by Goodenough (1968), no longer exists. The shortening of the $\text{Co}^{3+}-\text{O}^{2-}$ distance expected to accompany the transition from high- to low-spin states is barely detectable within the accuracy of this work, and can only be slight. This result may simplify the study of catalytically active surfaces, where the spin state of cobaltic ions may vary with fluctuations in the strength of the local crystal field. Even if this occurs, disturbances of the surface geometry are not to be expected.

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