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A high-temperature crystal modification of KO_2.

By GILES F. CARTER, JOHN L. MARGRAVE* and DAVID H. TEMPLETON, *Radiation Laboratory and Department of Chemistry and Chemical Engineering, University of California, Berkeley, California, U.S.A.*

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Recent observations (Carter, 1952) have indicated that crystals of NaO_2 undergo transitions at low temperatures from the random cubic structure proposed by Dauben & Templeton (1950) to ordered structures more similar to the tetragonal room-temperature form of KO_2 (Kassotoschkin & Kotow, 1936). Samples of KO_2 sealed in glass capillaries were studied in high-temperature diffraction cameras at temperatures up to 150° C. to see if a transition might be observed. X-ray powder patterns were obtained which indicate that a transition does occur in the region 60–100° C. to a cubic form. This transition is not rapidly reversible since the high-temperature form may be easily quenched to room temperature to give a mixture of the cubic and tetragonal forms.

Table 1. *Diffraction data for* KO_2 *(cubic form)* Cu $K\alpha$ radiation; $\lambda = 1{\cdot}5418$ Å

hkl	I_c	I_o	d (Å)
111	4·9	5·4	3·50
200	41·0	41	3·04
220	17·3	14	2·16
311	5·8	4·5	1·83
222	4·8	4·5	1·76
400	1·3	—	—
331	3·2	3·2*	1·40
420	3·1	3·2*	1·36
422	2·3	—	—
333	0·6	—	—
511	2·8		
440	0·8	—	—

* Near limit of detection.

From the data obtained one may calculate $a = 6{\cdot}09 \pm 0{\cdot}01$ Å for this new phase. Values for the interplanar distances, d, and intensities, as observed visually and as calculated, are given in Table 1. The unit-cell volume is 226 Å^3 as compared with 220 Å^3 ($a = 5{\cdot}71$ Å, $c = 6{\cdot}76$ Å) for the tetragonal form.

The observed intensities are in good agreement with those calculated for a NaCl-type structure having an O_2^- in each halide position with disorderly orientation, like structure (3) proposed for the room-temperature form of NaO_2 (Dauben & Templeton 1950). If the O_2^- are ordered, then a few extra lines should be above the limit of detection, though not by large factors, while the intensities of the observed lines are not changed significantly. Thus the disordered structure seems more probable.

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X-ray diffraction study of limonite.

By D. R. DASGUPTA and J. C. MAITRA, *Indian Association for the Cultivation of Science, Calcutta* 32, *India.*

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Standard books on mineralogy (Dana & Hurlbut, 1947, p. 208; Read, 1946, p. 463; Rogers & Kerr, 1942, p. 206) describe limonite as amorphous. It is a hydrated oxide of iron and is, according to Alexander (1931), mainly an aged gel. Accordingly one might except it to be of crystalline nature. However, no X-ray diffraction study of natural limonite has yet been reported. Products obtained by heating limonite to high temperatures were studied by Endô (1936) by the X-ray diffraction method but it is not known what those products are or whether they contain limonite. The present study has been undertaken to elucidate the atomic structure of limonite.

A sample of limonite from Gosalpur (Jubbulpur) was powdered and a rod of diameter less than 0·5 mm. was made with collodium as a binder. The rod was mounted on the axis of a cylindrical camera. X-rays from a Hadding tube fitted with iron anticathode and run at about 50 kV. and 5–7 mA. were used. The powder diagram gave the spacings d shown in Table 1. The sample was studied spectroscopically and the spectrogram revealed the pre-

Table 1. *Spacings and intensities of powder lines*

θ	d (Å)	Intensity
11° 18′	4·937	*w*
13° 18′	4·205	*vs*
13° 43′	4·080	*vw*
16° 31′	3·402	*w*
20° 50′	2·719	*ms*
22° 59′	2·414	*s*
25° 9′	2·276	*w*
25° 50′	2·220	*w*
28° 22′	2·035	*vw*
31° 58′	1·827	*vw*
33° 24′	1·758	*ms*
35° 13′	1·681	*vw*
36° 39′	1·620	*vw*
37° 45′	1·580	*w*
39° 9′	1·531	*w*
41° 18′	1·466	*vw*
42° 24′	1·434	*vw*
44° 33′	1·378	*w*
46° 21′	1·343	*w*