

Acta Cryst. (1952). **5**, 851

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.*

(Received 17 July 1952)

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

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.

From the data obtained one may calculate $a = 6.09 \pm 0.01 \text{ \AA}$ 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 \AA^3 as compared with 220 \AA^3 ($a = 5.71 \text{ \AA}$, $c = 6.76 \text{ \AA}$) 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.

This research was supported by the United States Atomic Energy Commission.

Table 1. *Diffraction data for KO_2 (cubic form)*
Cu $K\alpha$ radiation; $\lambda = 1.5418 \text{ \AA}$

| <i>hkl</i> | I_c | I_o | $d \text{ (\AA)}$ |
|------------|-------|-------|-------------------|
| 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.

if a transition might be observed. X-ray powder patterns were obtained which indicate that a transition does occur in the region $60\text{--}100^\circ\text{C}$. to a cubic form. This transition

* Atomic Energy Commission Postdoctoral Fellow 1951–52.

References

- CARTER, G. F. (1952). Dissertation, University of California, Berkeley.
 DAUBEN, C. H. & TEMPLETON, D. H. (1950). *J. Amer. Chem. Soc.* **72**, 2251.
 KASSOTOSCHKIN, W. & KOTOW, W. (1936). *J. Chem. Phys.* **4**, 458.

Acta Cryst. (1952). **5**, 851

X-ray diffraction study of limonite. By D. R. DASGUPTA and J. C. MAITRA, *Indian Association for the Cultivation of Science, Calcutta 32, India.*

(Received 28 July 1952)

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 expect 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 Endó (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 | $d \text{ (\AA)}$ | Intensity |
|----------------|-------------------|-----------|
| $11^\circ 18'$ | 4.937 | <i>w</i> |
| $13^\circ 18'$ | 4.205 | <i>vs</i> |
| $13^\circ 43'$ | 4.080 | <i>vw</i> |
| $16^\circ 31'$ | 3.402 | <i>w</i> |
| $20^\circ 50'$ | 2.719 | <i>ms</i> |
| $22^\circ 59'$ | 2.414 | <i>s</i> |
| $25^\circ 9'$ | 2.276 | <i>w</i> |
| $25^\circ 50'$ | 2.220 | <i>w</i> |
| $28^\circ 22'$ | 2.035 | <i>vw</i> |
| $31^\circ 58'$ | 1.827 | <i>vw</i> |
| $33^\circ 24'$ | 1.758 | <i>ms</i> |
| $35^\circ 13'$ | 1.681 | <i>vw</i> |
| $36^\circ 39'$ | 1.620 | <i>vw</i> |
| $37^\circ 45'$ | 1.580 | <i>w</i> |
| $39^\circ 9'$ | 1.531 | <i>w</i> |
| $41^\circ 18'$ | 1.466 | <i>vw</i> |
| $42^\circ 24'$ | 1.434 | <i>vw</i> |
| $44^\circ 33'$ | 1.378 | <i>w</i> |
| $46^\circ 21'$ | 1.343 | <i>w</i> |

sence of a small amount of titanium and silicon in addition to iron. Chemical analysis showed that the sample was composed of 84.44% Fe_2O_3 , 5.78% SiO_2 and 10% H_2O .

Identical X-ray diffraction patterns were obtained from powders of a sample of limonite from Nepal and another from Alabama, U.S.A. This clearly shows that natural limonites are crystalline although incapable of forming single crystals of appreciable size. Further studies are being undertaken.

We thank Prof. K. Banerjee, Sircar Professor of Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, for his inspiring guidance

and Prof. N. N. Chatterjee, Head of the Department of Geology, Calcutta University for the samples of limonite.

References

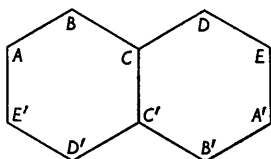
- ALEXANDER, J. (1931). *Colloid Chemistry*. New York: Reinhold.
 DANA, E. S. & HURLBUT, C. S. (1947). *Manual of Mineralogy*. New York: Wiley.
 ENDŌ, K. (1936). *Sci. Rep. Tôhoku Univ.* **25**, 913.
 READ, H. H. (1946). *Elements of Mineralogy*. London: Murby.
 ROGERS, A. F. & KERR, P. F. (1942). *Optical Mineralogy*. New York: McGraw-Hill.

Acta Cryst. (1952). **5**, 852

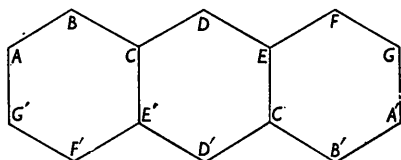
A refinement of the crystal and molecular structures of naphthalene and anthracene. By F. R. AHMED and D. W. J. CRUICKSHANK, *Chemistry Department, The University, Leeds 2, England*

(Received 31 July 1952)

Very complete redeterminations of the crystal and molecular structures of naphthalene (Abrahams, Robertson & White, 1949 *a, b*)



and of anthracene (Mathieson, Robertson & Sinclair, 1950; Sinclair, Robertson & Mathieson, 1950)



have been described recently. In these investigations the carbon co-ordinates were determined from triple Fourier series of observed structure factors evaluated at points throughout the unit cell. No attempt was made to correct the results for the effects of finite series, which were expected to be small; though in the three-dimensional analysis of the hydrocarbon dibenzyl (Jeffrey, 1947) the effects were shown to produce bond-length errors as large as 0.037 Å (Cruickshank, 1949). A detailed estimate of the accuracy of the results is also desirable for the comparison of the experimental bond lengths with quantum-mechanical calculations of Coulson, Daudel & Robertson (1951).

We have now made finite-series corrections to the naphthalene and anthracene bond lengths by Booth's (1945, 1946 *a*) back-correction method. Differential syntheses (Booth, 1946 *b*) were computed with the observed and calculated structure factors given by Robertson and his co-workers, all six second differentials being computed for each atom. From these syntheses

new atomic positions were found, from which the bond lengths given in Tables 1 and 2 were derived. The results of Robertson *et al.* are given for comparison. The finite-series corrections average 0.0058 Å per co-ordinate for each molecule, about half that for dibenzyl. The estimated standard deviations (e.s.d.) of the bond lengths are also shown in Tables 1 and 2, and were calculated by Cruickshank's (1949) method using $|F_o - F_c|$ as an estimate of $\sigma(F)$. The chemically equivalent but crystallographically non-equivalent bonds all agree within the e.s.d.'s, and so weighted mean estimates of the chemically independent bonds may be derived. These are given in Tables 3 and 4,

Table 1. *Bond lengths in naphthalene*

| Bond | Present refinement | E.s.d. | Robertson <i>et al.</i> |
|------|--------------------|---------|-------------------------|
| AB | 1.369 Å | 0.010 Å | 1.363 Å |
| BC | 1.426 | 0.007 | 1.421 |
| CD | 1.424 | 0.009 | 1.420 |
| DE | 1.362 | 0.008 | 1.354 |
| AE' | 1.404 | 0.009 | 1.395 |
| CC' | 1.393 | 0.010 | 1.395 |

Table 2. *Bond lengths in anthracene*

| Bond | Present refinement | E.s.d. | Robertson <i>et al.</i> |
|------|--------------------|---------|-------------------------|
| AB | 1.365 Å | 0.009 Å | 1.361 Å |
| BC | 1.428 | 0.007 | 1.426 |
| CD | 1.393 | 0.007 | 1.387 |
| DE | 1.398 | 0.006 | 1.395 |
| EF | 1.418 | 0.008 | 1.412 |
| FG | 1.375 | 0.007 | 1.366 |
| AG' | 1.408 | 0.010 | 1.390 |
| CE' | 1.436 | 0.007 | 1.440 |

together with their e.s.d.'s (allowance has been made for the negative correlation of the lengths of BC and CD in naphthalene through the common atom C, and similarly for CD and DE in anthracene).

Tables 3 and 4 also give the theoretical bond lengths according to the molecular orbital calculations of Coulson