

## SHORT COMMUNICATIONS

### ACCURATE UNIT CELL DIMENSIONS OF HEMATITE ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)\*

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Measurements recently made by the authors have yielded cell dimensions of hematite which are significantly different from the presently accepted values given by Aravindakshan and Ali,<sup>1</sup> which are quoted on card 13-534 of the Powder Diffraction Index published by the American Society for Testing and Materials.

#### Experimental

Spectrographically pure hematite powder‡ was used and mixed with a sample of standardized silicon powder obtained from Dr W. Parrish, Philips Laboratories, Irvington-on-Hudson, New York, U.S.A., in the ratio of three parts of hematite to one part of silicon. The mixture was packed into Lindemann glass tubes of 0.5 mm diameter, and photographs were taken with a Philips PW1024 114.83-mm diameter camera on a Philips 1008 half-wave rectified X-ray generator, using iron-filtered Co K $\alpha$  radiation. The photographs were taken at room temperature (20°).

The accurately known  $\theta$ -values of the 440 and 531 reflections of silicon provided an internal calibration of the films, thus minimizing systematic errors. Four reflections of hematite with  $\theta > 70^\circ$  were used and eight films were exposed.

The reflections were from the (140), (413), (048), and the (1310) planes, indexed on the hexagonal system. Each  $\alpha_1$  and  $\alpha_2$  line was measured, yielding a total of 103 reliable  $\theta$  values for use in a least-squares computation. Each  $\theta$  value was the average of six individual measurements.

*Standards used.*— $\lambda$  (Co K $\alpha_1$ ) = 1.78892 Å;  $\lambda$  (Co K $\alpha_2$ ) = 1.79278 Å.

For Si line 440:  $\theta$ (Co K $\alpha_1$ ) = 68.707°;  $\theta$ (Co K $\alpha_2$ ) = 69.027°.

For Si line 531:  $\theta$ (Co K $\alpha_1$ ) = 77.016°;  $\theta$ (Co K $\alpha_2$ ) = 77.563°.

#### Results

Present Work	Aravindakshan and Ali
$a_0 = 5.0340 \pm 0.0007$ Å	$a_0 = 5.0317$ Å
$c_0 = 13.752 \pm 0.003$ Å	$c_0 = 13.737$ Å

(Errors are three times the standard deviation.)

#### Discussion

It is thought that the claim of five significant figures in the work of Aravindakshan and Ali is somewhat overoptimistic, since it was "based on careful  $d$  measurements of the standard hematite pattern, after checking for film shrinkage". In the opinion of the authors, such a procedure could not accurately yield more than three significant figures, and to this level the two sets of results are in agreement. The fourth and fifth significant figures of Aravindakshan and Ali are therefore thought to be in error,

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‡ Johnson, Matthey & Co. "Specpure" iron oxide. The certified report gives impurities as: Si, 2 p.p.m.; Mn, 1 p.p.m.; Mg, 1 p.p.m.; Cu < 1 p.p.m.; Ag < 1 p.p.m.

<sup>1</sup> Aravindakshan, C., and Ali, S. Z., *J. scient. ind. Res. B*, 1962, **21**, 316.

especially since no chemical purity of their hematite is given. It is believed that these new values are more accurate, within the specified errors, for the following reasons:

(1) The internal standard used ensures that all known systematic errors will be minimized. Silicon was studied in an international project,<sup>2</sup> and the mean cell size and the standard deviation were found to be  $a = 5.43054 \text{ \AA}$ ;  $\sigma = 0.00017 \text{ \AA}$ . Taking the error to be three times the standard deviation, this represents an accuracy of about 1 in  $10^4$ . The  $\theta$  values given above for silicon 440 and 531 lines were calculated from this cell parameter. The values of the wavelengths were taken from International Tables for X-ray Crystallography.<sup>3</sup>

(2) The least-squares computer programme was written in PL1 computing language for a 360/50 I.B.M. computer. It was based on standard statistical procedure (e.g.<sup>4</sup>) and was tested on a simulated hexagonal crystal with "ideal" cell parameters  $a_0 = 5.6100 \text{ \AA}$ ;  $c_0 = 10.000 \text{ \AA}$ . Bragg angles based on these dimensions were calculated for a large number of indices, and 200 reflections with  $\theta > 70^\circ$  were selected. The values of the angles were changed randomly within the approximate limits of  $\pm 0.15^\circ$ . These data were then used for the computation of cell dimensions, and the returned values were  $a_0 = 5.6099 \pm 0.0003 \text{ \AA}$ ;  $c_0 = 9.9999 \pm 0.0010 \text{ \AA}$ .

One of the features of the programme is the direct linearization of the observational equations, in terms of squares of the reciprocal parameters. The required cell dimensions and their errors are then calculated analytically from the adjustable parameters and their estimated standard deviations. Direct linearization removes the necessity for providing approximate initial values of the parameters to be calculated, and avoids the danger that the function to be minimized in a least-squares procedure will settle into a local minimum.

All the measurements were assumed to be of equal reliability, and for the least-squares computation were weighted according to the expression  $W = \lambda^4/\sin^2 2\theta$  deduced by Grainger.<sup>5</sup> Copies of the programme may be obtained from the authors.

#### *Acknowledgments*

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<sup>2</sup> Parrish, W., *Acta crystallogr.*, 1960, **13**, 838.

<sup>3</sup> "International Tables for X-ray Crystallography." Vol. III. (Kynoch Press: Birmingham 1962.)

<sup>4</sup> Hamilton, W. C. "Statistics in Physical Science." (Ronald Press: New York 1964.)

<sup>5</sup> Grainger, C. T., Thesis, University of New South Wales, 1967.