14·026 Å. Analysis of the lattice images from these areas showed hematite/ilmenite (*h/i*) lamellae about 30–300 Å wide in magnetite–ulvöspinel with a growth habit of $(111)_m \parallel (0001)_{h/i}$ as shown in the examples of Figs. 6(*a*) and (*b*), the direction of growth being similar to that observed in the natural ilmenite samples. However, in some samples during slow oxidation experiments conducted for several hours at lower temperatures, it was possible to observe the growth along $[100]_m$ indicating the replacement of the ulvöspinel phase (Frost, 1979).

In the oxidation reactions described it seems likely that both Fe_3O_4 and Fe_2TiO_4 undergo partial oxidation. The close similarity in the structures of the phases makes it difficult to differentiate between the nature of the oxidation process governing the two phases at different temperatures within the small areas (<200–300 Å) of the crystals. Under these conditions the incorporation of oxygen in magnetite–ulvöspinel can be simply written as

$$3Fe_2TiO_4 + \tfrac{1}{2}O_2 \rightarrow 3FeTiO_3 + Fe_3O_4,$$

$$2Fe_2TiO_4 + \tfrac{1}{2}O_2 \rightarrow 2FeTiO_3 + Fe_2O_3$$

and

$$2Fe_3O_4 + \tfrac{1}{2}O_2 \rightarrow 3Fe_2O_3.$$

Conclusions

The Fe_3O_4–Fe_2TiO_4 natural mineral consists of cubes of magnetite and lamellae of ulvöspinel with two sets of edge dislocations at the boundaries of the two phases generated during the subsolidus exsolution. The direct observations of oxidation experiments on these minerals have revealed that a cation-deficient cubic intermediate phase may sometimes occur in the oxidation of magnetite–ulvöspinel to rhombohedral hematite–ilmenite. When the oxidation temperature is >873 K, hematite/ilmenite lamellae grow into the magnetite–ulvöspinel with the $(111)_m \parallel (0001)_{h/i}$ habit.

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Absorption and Extinction Corrections: Standard Tests

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Abstract

The standard-test tables of values of transmission factors and $\bar{T}$, the absorption-weighted mean path lengths, given by Cahen & Ibers [*J. Appl. Cryst.* (1972), **5**, 298–299; *J. Appl. Cryst.* (1973), **6**, 244] and Alcock [*Acta Cryst.* (1974), A**30**, 332–335] have been corrected and extended.

Introduction

A difficult problem in producing a computer program is that of making sure that it is thoroughly tested. We

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have been confronted with this problem in using absorption-correction programs and have found that published standard tests can be exceedingly useful.

In the literature, there are two sets of results which may be used in testing absorption-correction programs. These are due to Cahen & Ibers (1972, 1973), hereafter CI, and to Alcock (1974), hereafter AL.

CI give the values of transmission factors for a crystal in the form of a trigonal prism with a cross section of an isosceles triangle (lengths of sides x, x, $\sqrt{2}x$). For an infinitely long crystal, CI give analytical expressions for the transmission factors of two reflections when the crystal is in one special orientation. No values of $\bar{T}$, the absorption-weighted mean path length, are given.

AL gives transmission factors and $\bar{T}$ values for a crystal without a morphological centre of symmetry for various types of camera and diffractometer geometry. There are several typographical errors in these results, and they do not include data for azimuthal scans on a four-circle diffractometer.

We present here selected tables* of values which supplement and correct the values of CI and AL. We have two programs at our disposal (XRAY System; Stewart, 1976). One is a Gaussian grid integration program (Busing & Levy, 1957) and the other uses the

* Extensive tables of values of transmission factors and $\bar{T}$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35136 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Characteristics of calculation methods for CI's crystal test*

		Method 2	Method 3			Method 4
Numerical method		Gaussian grid $12 \times 12 \times 32$	Analytical technique (de Meulenaer & Tompa, 1965)			Evaluation of expression derived by method of Evans (1952)
Length of crystal (L)		$20x$	$20x$			∞
$\bar{T}$ calculation		Numerical integration of $\bar{T}$	$T = -\frac{1}{A}\frac{\Delta A}{\Delta \mu}$			Formulae in text
			3(a) $\Delta\mu = 0{\cdot}01\,\mu$	3(b) $\Delta\mu = 0{\cdot}001\,\mu$	3(c) $\Delta\mu = 0{\cdot}0001\,\mu$	
Floating-point variable representation	No. of bits for exponent	8		11		7
	No. of bits for mantissa	28		61		57
	Total no. of bits	36		72		64

Table 2. *Values of* $\bar{T}$ ($\times 10^3$ mm) *for CI's crystal test*

The characteristics of the different methods are given in Table 1. The crystal shape, orientation and A values can be found in CI.

Reflection	x (mm)	μ (mm^{-1})	Method 2	Method 3(a)	Method 3(b)	Method 3(c)	Method 4
$\bar{1}\,1\,0$	10·0	10·0	119·9	98·5	99·4	99·5	99·5
		1·0	947·4	938·5	946·5	947·3	947·4
		0·1	4768	4749	4766	4768	4768
		0·01	6447	6444	6447	6448	6448
$\bar{1}\,1\,0$	0·5	100·0	10·0	9·8	9·9	9·9	9·9
		10·0	88·9	88·1	88·8	88·9	88·9
		1·0	281·7	281·1	281·7	281·7	281·7
		0·1	327·8	327·7	327·8	327·8	327·8
$1\,\bar{1}\,0$	10·0	10·0	219·0	197·0	199·7	200·0	200·0
		1·0	1995	1966	1992	1995	1996
		0·1	6078	6056	6076	6078	6078
		0·01	6611	6608	6611	6611	6611
$1\,\bar{1}\,0$	0·5	100·0	20·0	19·7	20·0	20·0	20·0
		10·0	182·4	180·2	182·2	182·4	182·5
		1·0	319·0	318·4	318·9	319·0	319·0
		0·1	331·9	331·9	331·9	331·9	331·9

analytical method (de Meulenaer & Tompa, 1965; Alcock, 1970). The machine precision can be inferred from Table 1.

In the analytical-method program, where $\bar{T}$ is calculated from

$$\bar{T} = -\frac{1}{A}\frac{\Delta A}{\Delta \mu},$$

the value of $\Delta\mu$ has to be a compromise between a small value for accuracy and a larger value to avoid indeterminacy and errors in calculating ΔA by subtraction $[A(\mu + \Delta\mu) - A(\mu)]$. Thus $\Delta\mu$ has to be chosen as a function of the machine precision. In the tests with CI's crystal, $\bar{T}$ values for three different values of $\Delta\mu$ are given. In all subsequent tests $\Delta\mu$ was fixed at 0·0001 μ.

CI's crystal test

Both our programs give transmission values identical to those of CI. Tables 1 and 2 give our results for the absorption-weighted mean path length ($\bar{T}$). The formulae in method 4 are obtained by differentiation of the expressions of CI with

$$\bar{T} = -\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}\mu}.$$

We obtain

$$\bar{T}(1\bar{1}0) = \frac{\mu^{-1}[(x^2\mu^2 + 2x\mu + 2)\exp(-\mu x) - 2]}{(x\mu + 1)\exp(-\mu x) - 1},$$

$$\bar{T}(\bar{1}10) = \frac{2\mu^{-1}[(x\mu + 1)\exp(-2\mu x) + \mu x - 1]}{\exp(-2\mu x) + 2\mu x - 1}.$$

AL's irregular-crystal test

Transmission factors and $\bar{T}$ values were calculated for the crystal and camera geometries indicated in Table 1 of AL. The Gaussian grid was $N \times N \times N$ with $N = 16$, 24 and 32. All values obtained are included in the deposited Supplementary Publication.* Satisfactory agreement was obtained between the results from our Gaussian-grid program, our analytical-method program and the transmission factors given in Table 1 of AL apart from the following typographical errors.

(*a*) The direction cosine to *OZ* for 0 −2 1 should be 0·4222 and not 0·4216.

(*b*) The transmission factors ($\times 10^4$) for μ = 1·0, normal beam *Y* upper-side geometry for 1 −2 3 and −1 2 −3 should be 3317 and not 3137.

* See previous footnote.

(*c*) The transmission factors for μ = 1·0, precession 30° angle *X* (precession axis) have been calculated for λ = 0·7107 and not λ = 1·542 Å. The reflections −1 2 3, −1 2 −3, −1 −2 3 and −1 −2 −3 are observable for λ = 0·7107 but not for λ = 1·542 Å.

(*d*) The heading for the diffractometer recording should read: φ = 0·0 if χ = 90·0, and not φ = 0·0 if χ = 0·0.

For comparison we give in Table 3 the transmission factors obtained for AL's four-circle diffractometer.

Satisfactory agreement was also obtained amongst our methods of calculating $\bar{T}$. However, these results are at variance with those given in AL's Table 3. As we were working with a greater machine precision than AL, a smaller value of $\Delta\mu$ could be used giving more accurate values of $\bar{T}$. In Table 4 we present values of $\bar{T}$ for the four-circle diffractometer geometry. In Table 5 a

Table 3. *Transmission factors* ($\times 10^4$) *for AL's irregular crystal on a four-circle diffractometer*

Orientation and cell information are given in AL Table 1.

			Gaussian grid $N \times N \times N$			
h	*k*	*l*	$N = 16$	$N = 24$	$N = 32$	Analytical method
0	1	1	3344	3349	3349	3349
0	0	1	3391	3397	3397	3397
0	0	−1	3392	3396	3397	3397
1	2	3	3200	3197	3201	3200
1	2	−3	1667	1681	1679	1680
1	−2	3	2553	2563	2562	2563
1	−2	−3	3353	3357	3358	3358
−1	2	3	3351	3357	3357	3358
−1	2	−3	2646	2659	2658	2658
−1	−2	3	1764	1774	1773	1773
−1	−2	−3	3173	3175	3175	3175

Table 4. $\bar{T}$ *values for AL's irregular crystal on a four-circle diffractometer*

Orientation and cell information are given in AL Table 1.

			Gaussian grid $N \times N \times N$			
h	*k*	*l*	$N = 16$	$N = 24$	$N = 32$	Analytical method
0	1	1	1·003	1·001	1·001	1·001
0	0	1	0·9806	0·9787	0·9785	0·9784
0	0	−1	0·9803	0·9788	0·9785	0·9784
1	2	3	1·014	1·015	1·014	1·014
1	2	−3	1·417	1·404	1·406	1·405
1	−2	3	1·145	1·140	1·140	1·140
1	−2	−3	0·9942	0·9931	0·9925	0·9926
−1	2	3	0·9953	0·9927	0·9927	0·9926
−1	2	−3	1·076	1·070	1·071	1·070
−1	−2	3	1·308	1·298	1·299	1·299
−1	−2	−3	1·033	1·032	1·032	1·032

Table 5. *Extinction correction*

Orientation and cell information are given in AL Table 1.

	Equi-inclination crystal l, rotation axis X			Diffractometer		
				Diffracto-meter	No mono-chromator	Mono-chromator
	$\mu = 1{\cdot}0$	$\mu = 0{\cdot}15$	$\mu = 0{\cdot}01$	$\mu = 1{\cdot}0$		$\alpha = 35°$ $\beta = 0°$
h k l	$\bar{T}$	$\bar{T}$	$\bar{T}$	$\bar{T}$	$10^6\,\delta/\bar{T}$	$10^6\,\delta/\bar{T}$
0 1 1	1·245	1·837	1·940	1·001	1781	1773
0 0 1	1·229	1·722	1·808	0·9784	2916	2911
0 0 −1	1·229	1·722	1·808	0·9784	2916	2911
1 2 3	1·098	1·714	1·827	1·014	577	555
1 2 −3	1·319	1·940	2·051	1·405	749	731
1 −2 3	1·323	1·960	2·075	1·140	749	731
1 −2 −3	1·263	1·783	1·873	0·9926	720	702
−1 2 3	1·235	1·778	1·872	0·9926	720	702
−1 2 −3	1·272	1·951	2·075	1·070	749	731
−1 −2 3	1·319	1·940	2·051	1·299	749	731
−1 −2 −3	1·239	1·741	1·829	1·032	577	555

Table 6. *Transmission factors* ($\times 10^4$) *and* $\bar{T}$ *values for AL's irregular crystal on a four-circle diffractometer*

Orientation and cell information are given in AL Table 1. $N = 16$, $N = 24$ indicate results of a Gaussian-grid integration $N \times N \times N$. AM indicates analytical method.

	$\mu = 0{\cdot}01$	$\mu = 0{\cdot}1$	$\mu = 10{\cdot}0$	$\mu = 10{\cdot}0$
h k l	$N = 16$	$N = 24$	$N = 24$	AM
Transmission factors ($\times 10^4$)				
0 1 1	9883	8895	83	84
0 0 1	9883	8899	74	75
0 0 −1	9883	8899	74	75
1 2 3	9875	8828	105	106
1 2 −3	9785	8074	27	26
1 −2 3	9842	8549	52	53
1 −2 −3	9882	8891	71	71
$\bar{T}$ values				
−1 2 3	1·183	1·167	0·195	0·194
−1 2 −3	1·588	1·537	0·133	0·132
−1 −2 3	2·173	2·091	0·124	0·124
−1 −2 −3	1·256	1·236	0·194	0·194

Table 7. *Transmission factor* ($\times 10^4$) *and* $\bar{T}$ *values for AL's irregular crystal* (μ = 1·0) *on a four-circle diffractometer*

Values have been calculated with the analytical method. Orientation and cell information are given in AL Table 1. The 1 −2 −3 reflection was used.

ψ (°) or ψ + 180 (°)	Transmission factor ($\times 10^4$)	$\bar{T}$
0	3358	0·9926
10	3291	0·9939
20	3140	1·014
30	2907	1·054
40	2591	1·121
90	2119	1·254
140	2811	1·183
150	2988	1·138
160	3214	1·058
170	3334	1·012

Table 8. *Directional components* ($\times 10^5$) *with respect to the direct crystal axes for selected geometries*

Orientation and cell information are given in AL Table 1.

h k l	Incident ray			Diffracted ray			Recording method
0 1 1	−9036	−3984	2481	−8192	−2338	3842	Diffractometer $\psi = 0°$
0 1 1	−10300	−1820	316	−9456	−173	1677	Diffractometer $\psi = 23°$
1 −2 3	−7499	−7650	−5141	−5714	−9361	−1795	Diffractometer $\psi = 0°$
1 −2 3	−9802	−6267	−3451	−8017	−7978	−105	Diffractometer $\psi = 23°$

Table 9. *Calculated volumes in units as D of Alcock's irregular crystal*

Axial summation order			Gaussian grid $N \times N \times N$			Analytical method
Slow	Medium	Fast	$N = 16$	$N = 24$	$N = 32$	
a	b	c	8499·1	8510·8	8509·6	8510·5
b	c	a	8501·8	8504·5	8515·5	8510·5
c	a	b	8510·0	8514·3	8509·9	8510·5

complete new version of AL's Table 3 is shown which was calculated with the analytical-method program and $\Delta\mu = 0{\cdot}0001$. In relation to the last two columns in AL's Table 3, it should be pointed out that AL's equation (6) should read

$$P_n = 0{\cdot}5[(\cos^2\beta + \sin^2\beta\cos^2\alpha) + (\sin^2\beta + \cos^2\beta\cos^2\alpha)\cos^{2n}2\theta].$$

It was decided that more tests would be desirable for the four-circle diffractometer geometry. Hence we also carried out AL's irregular crystal test for (1) values of μ = 0·01, 0·1, 1·0, 10·0 and 100·0 and (2) for the reflections 1 2 3 and 1 −2 −3, μ = 1·0, for azimuthal angles in the range 0 to 360° calculated in steps of 10°. A resumé of the values obtained is given in Tables 6 and 7. Positive ψ corresponds to an anti-clockwise rotation when looking along the normal to the reflecting plane towards the crystal. $\psi = 0$ is defined by the bisecting position of $\omega = \theta$. As a help for checking programs we give in Table 8 directional components of unit vectors in the direction of the incident and reflected beams. These components are with respect to the direct crystal axes. Another useful check on a program is the volume calculated for the crystal. These values are given in Table 9.

AL's regular crystal test

We obtained the same values as in AL's Table 2. Our complete results may be found in the Supplementary Publication.

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The Critical-Voltage Effect in Convergent-Beam High-Voltage Electron Diffraction

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Abstract

The critical-voltage effect has been combined with the convergent-beam electron diffraction technique using a high-voltage electron microscope. The method allows the critical voltage V_c to be detected to within approximately ±1 kV, compared with ±5 kV in previous methods. This accuracy is achievable throughout the 100 to 1000 kV accelerating-voltage range of the high-voltage microscope used. V_c has also been determined by varying the specimen temperature at constant voltage, which has the advantage that all electron-optical parameters are kept constant: thus the 'transfer function' of the microscope is constant. The critical voltage is easily identified experimentally by the appearance of a characteristic 'dark band' in the Bragg-satisfied second-order convergent-beam disc. Changes in the asymmetry of the Kikuchi line within the dark band enable the precise localization of V_c to ±1 kV to be made. The improved precision of this new method considerably increases its application to the determination of scattering factors in pure materials and to ordering and electron-transfer effects in certain alloys. The method is illustrated by applying it to Cu and Cu–Al alloys.

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