respect to s. By this procedure one obtains the parameters

$$\sum_s K(s, \Delta u).f(s) = F(\Delta u), \qquad (7)$$

specified in Table 2 by boxes.

(3) Henceforth, with regard to the relation of

$$\sum_{\Delta u} F(\Delta u)(1-x)^{-\Delta u} = U \qquad (8)$$

to equation (5) the calculation of U is easily completed.

Selecting, for example, the probability ${}^2P_7^{(3)}$ one obtains from Table 2(a)

$$U_7^{(3)} = 62 + 60(1-x)^{-1} + 3(1-x)^{-2}. \qquad (9)$$

Taking $w_7^{(3)} = 9$ the complete numerical expression

$${}^2P_7^{(3)} = 7x^6(1-x)^7[62(1-x)^2 + 60(1-x) + 3] \quad (10)$$

is obtained from equation (3).

References

Férey, G., de Pape, R. & Boucher, B. (1978). *Acta Cryst.* B**34**, 1084–1091.
Friebel, C. (1974). *Z. Naturforsch. Teil B*, **29**, 634–641.
Friebel, C., Propach, V. & Reinen, D. (1976). *Z. Naturforsch. Teil B*, **31**, 1574–1584.
Friebel, C. & Reinen, D. (1969). *Z. Naturforsch. Teil A*, **24**, 1518–1525.
Friebel, C. & Reinen, D. (1974). *Z. Anorg. Allg. Chem.* **407**, 193–200.
Goodyear, J., Ali, E. M. & Sutherland, H. H. (1979). *Acta Cryst.* B**35**, 456–457.
Hoggins, J. T. & Steinfink, H. (1977). *Acta Cryst.* B**33**, 673–678.
Hottentot, D. & Loopstra, B. O. (1979). *Acta Cryst.* B**35**, 728–729.
Jeitschko, W. & Sleight, A. W. (1974). *Acta Cryst.* B**30**, 2088–2094.
Kato, K. & Kawada, I. (1977). *Acta Cryst.* B**33**, 3437–3443.
Kaučič, V. & Bukovec, P. (1978). *Acta Cryst.* B**34**, 3337–3339.
Krause, S. & Reinen, D. (1979). To be published.
Krebs, B., Henkel, G. & Dartmann, M. (1979). *Acta Cryst.* B**35**, 274–278.
Lazarini, F. (1977). *Acta Cryst.* B**33**, 2961–2964.
Reinen, D. (1968). *Z. Naturforsch. Teil A*, **23**, 521–529.
Reinen, D. & Friebel, C. (1979). *Struct. Bonding (Berlin)*, **37**. 1–60.
Reinen, D. & Grefer, J. (1973). *Z. Naturforsch. Teil A*, **28**, 1185–1192.
Reinen, D. & Weitzel, H. (1977). *Z. Naturforsch. Teil B*, **32**, 476–478.
Ribes, M., Olivier-Fourcade, J., Philippot, E. & Maurin, M. (1974). *Acta Cryst.* B**30**, 1391–1395.
Rieck, H. & Hoppe, R. (1972). *Z. Anorg. Allg. Chem.* **392**, 193–196.
Rieck, H. & Hoppe, R. (1973). *Z. Anorg. Allg. Chem.* **400**, 311–320.
Schnering, H. G. von (1967). *Z. Anorg. Allg. Chem.* **353**, 13–25.
Schnering, H. G. von (1973). *Z. Anorg. Allg. Chem.* **400**, 201–207.
Taguchi, H., Takeda, Y., Kanamaru, F., Shimada, M. & Koizumi, M. (1977). *Acta Cryst.* B**33**, 1299–1301.
Vlasse, M., Matejka, G., Tressaud, A. & Wanklyn, B. M. (1977). *Acta Cryst.* B**33**, 3377–3380.
Wells, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed. Oxford: Clarendon Press.
Zabel, M. & Range, K.-J. (1979). *Z. Naturforsch. Teil B*, **34**, 1–6.

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Temperature Dependence of the Atomic Thermal Displacements in UO$_2$: A Test Case for the Rietveld Profile-Refinement Procedure

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Abstract

The neutron diffraction powder pattern of UO$_2$ has been recorded at five temperatures between 293 and 1733 K, and the data have been analysed by two methods: the Rietveld profile-refinement procedure and the more conventional approach based on independent integrated intensities. The structural parameters (*i.e.* the thermal amplitudes of the U and O atoms) derived by the two methods do not differ significantly, but the e.s.d.'s of the parameters given by the Rietveld treatment differ at some temperatures from those obtained

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by the conventional analysis. These results are discussed in the light of the statistical analysis of the Rietveld procedure published by Sakata & Cooper [*J. Appl. Cryst.* (1979), **12**, 554–563]. At the higher temperatures, the observed mean-square displacements of the U atoms are larger than those calculated by Dolling, Cowley & Woods [*Can. J. Phys.* (1965), **43**, 1397–1413] from the analysis of room-temperature phonon dispersion curves.

1. Introduction

For the past ten years, the profile-refinement method of Rietveld (1967, 1969) has been widely used for the interpretation of neutron diffraction powder patterns; more recently, the procedure has been extended to the analysis of X-ray diffraction powder data (Young, Mackie & Von Dreele, 1977; Malmros & Thomas, 1977). Intensity points at small intervals in the diffraction pattern are treated as individual observations which may arise from contributions from a number of Bragg reflections, so that the profile-refinement method can be used even when there is a large number of overlapping peaks. On the other hand, in the more conventional refinement procedure the integrated intensities are derived by assuming that the Bragg reflections may be separated from one another; this approach cannot be used where there is severe overlapping of adjacent peaks.

Sakata & Cooper (1979) have carried out a statistical analysis of the Rietveld method and have raised a number of questions regarding its validity. In particular, they show that the crystallographic parameters derived by the two types of refinement are not necessarily the same, and that the e.s.d.'s of the parameters are different.

In the present paper we test these theoretical predictions by applying both refinement procedures to the same experimental measurements. The system we have chosen is polycrystalline UO_2, examined by neutron diffraction over a range of temperature from 293 to 1733 K. With a sufficiently long neutron wavelength and a high take-off angle at the monochromator, most of the Bragg peaks were well separated in the diffraction pattern. The scattering data could be analysed satisfactorily, therefore, by both methods.

2. Structure factors of uranium dioxide

UO_2 has the face-centred cubic fluorite structure, with U atoms at the 4(*a*) positions

$$000 + \text{f.c.c. translations}$$

of the *Fm*3*m* space group, and O atoms at the 8(*c*) positions

$$\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4},\tfrac{3}{4}\tfrac{3}{4}\tfrac{3}{4} + \text{f.c.c. translations.}$$

The structure factors, corrected for the effect of thermal motion, can be written

$$\begin{aligned} F(hkl) &= 4b_U \exp(-B_U \sin^2\theta/\lambda^2) \\ &\quad + 8b_O \exp(-B_O \sin^2\theta/\lambda^2) \\ &\qquad \ldots h+k+l=4n \\ &= 4b_U \exp(-B_U \sin^2\theta/\lambda^2) \\ &\qquad \ldots h+k+l=4n\pm 1 \\ &= 4b_U \exp(-B_U \sin^2\theta/\lambda^2) \\ &\quad - 8b_O \exp(-B_O \sin^2\theta/\lambda^2) \\ &\qquad \ldots h+k+l=4n+2. \end{aligned} \tag{1}$$

Here b_U (= $0{\cdot}84 \times 10^{-11}$ mm) and b_O (= $0{\cdot}58 \times 10^{-11}$ mm) are the coherent neutron scattering amplitudes of U and O respectively. B_U is given by

$$B_U = 8\pi^2\overline{u_U^2},$$

where $\overline{u_U^2}$ is the isotropic mean-square thermal displacement of the U atoms. ($\overline{u_U^2}$ is one-third of the total mean-square displacement in all directions.) Similarly, $B_O = 8\pi^2\overline{u_O^2}$. The expressions above require slight modifications to include anisotropic, anharmonic contributions to the Debye–Waller factors (Rouse, Willis & Pryor, 1968). However, the measurements analysed in this paper gave anharmonic thermal parameters which were not significantly different from zero, and so thermal anisotropy was not allowed for in the subsequent treatment. We see then that, at each temperature, there are just three structural parameters to be determined: the scale factor s, and the quantities B_U and B_O in the Debye–Waller factors.

According to Cooper & Sakata (1979) the best value of the ratio b_U/b_O is $1{\cdot}451 \pm 0{\cdot}002$. We have used a ratio of 1·448, which is sufficiently close to the recommended value to give essentially the same values for the final structural parameters.

3. Conventional refinement

The neutron powder diffraction pattern of UO_2 was recorded with the PANDA diffractometer installed at the PLUTO reactor, Harwell. The polycrystalline sample, of composition close to $UO_{2{\cdot}00}$, was enclosed in a cylindrical can of Ta. With a wavelength of 1·334 Å and a range of scattering angles of $18 < 2\theta < 114°$, all reflections up to 533 were observed. However, not all these reflections were included in the later analysis. 311, 222 and 400 were excluded because they overlapped with reflections from the Ta sample holder and furnace, while 333 and 511 were left out as they appeared together at the same 2θ.

The intensity in the pattern was measured at increments in 2θ of 0·1°, and the integrated intensity for each isolated Bragg peak determined by summing the counts, point-by-point, across the peak and subtracting the background on either side. The relation between the integrated intensity ρ from the sample and the observed structure factor F_o is

$$\rho(hkl) = \text{constant} \times \frac{VN_c^2 mF_o^2}{\sin\theta \sin 2\theta}, \qquad (2)$$

where V is the volume of the sample in the beam, N_c is the number of unit cells/mm³, and m is the multiplicity factor for the hkl plane (Bacon, 1976). The constant in (2) includes the wavelength of the neutron radiation and the absorption factor (which, in our case, is very nearly independent of θ).

(2) was used to establish relative values of F_o at the five temperatures 293, 1073, 1373, 1673 and 1733 K. A least-squares refinement was then carried out for each temperature, where the quantity

$$\sum_{hkl} w_{hkl} |(F_o^2 - sF_c^2|^2$$

was minimized to yield the scale factor s and the parameters $B_{\rm U}$ and $B_{\rm O}$. w_{hkl} is the weight of F_o^2 and was calculated from

$$w_{hkl} = \frac{1}{\sigma_{hkl}^2}, \; \sigma_{hkl} = F_o^2 \frac{(I+B)^{1/2}}{(I-B)}, \qquad (3)$$

where B is the background count and I is the integrated intensity count plus the background count. The computer program used for the refinement was *ORXFLS* 3 (Busing *et al.*, 1971).

Table 1 lists the three structural parameters, with their e.s.d.'s, as given by the formula

$$(\sigma_i^2)_I = (A_{ii}^{-1})_I \sum_{hkl} w_{hkl} |F_o^2 - sF_c^2|^2/(N_I - P_S). \qquad (4)$$

Here $(\sigma_i)_I$ is the e.s.d. of the ith parameter and A_{ii}^{-1} is the ith diagonal element of the inverted normal matrix A^{-1}. The subscript I refers to integrated intensity measurements, N_I is the number of independent integrated intensities, and $P_S(=3)$ is the number of structural parameters. We also give in Table 1 the residual $R(wF^2)$, defined by

$$R(wF^2) = \sum w|F_o^2 - sF_c^2|^2/\sum w|F_o^2|^2,$$

and the agreement factor A_B, defined by

$$A_B^2 = \sum w|F_o^2 - sF_c^2|^2/(N_I - P_S). \qquad (5)$$

The scale factor s shows a slight decrease with increasing temperature, so that the intensities measured at the highest temperature (1733 K) were about 5% less than those calculated with the room-temperature value of the scale factor. This effect can be explained in terms of the loss or gain of scattering material as the lattice expands or contracts. The specimen height was greater than the beam height, and so, because s is proportional to $V/V_{\rm cell}^2$ [see (2)], where V is the volume of the specimen in the beam and $V_{\rm cell}$ is the unit-cell volume, s varies as the inverse fourth power of the lattice parameter a_o. The temperature dependence of a_0 is given by (11) below.

In Figs. 1 and 2 we plot the observed B values for U and O (indicated by open circles) as a function of temperature, and compare them with the values calculated

Table 1. *Results given by the conventional refinement method (using integrated intensities)*

Temperature (K)	$B_{\rm U}$ (Å²)	$B_{\rm O}$ (Å²)	s (relative)	N_I	$R(wF^2)$ (%)	A_B
293	0·18 (10)	0·66 (12)	1·00 (2)	9	3·30	4·23
1073	0·91 (7)	1·68 (9)	0·96 (2)	9	1·99	2·01
1373	1·40 (5)	2·20 (6)	0·96 (1)	9	1·19	1·10
1673	1·68 (17)	2·79 (21)	0·96 (2)	8	3·40	3·24
1733	1·73 (10)	3·03 (14)	0·95 (2)	8	2·13	1·94

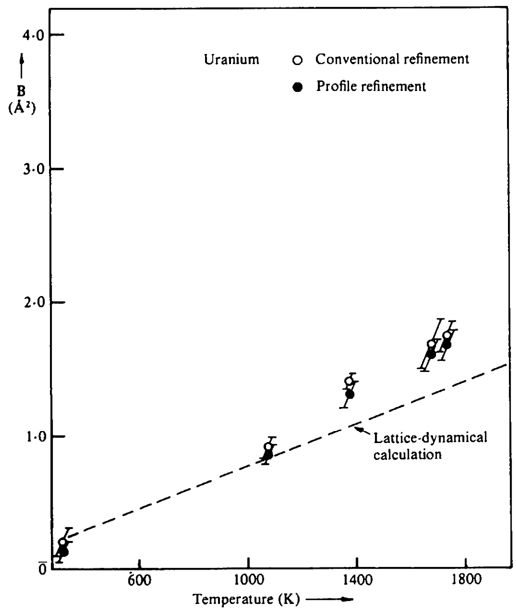

Fig. 1. Temperature dependence of the B values for U, as determined by the two refinement methods. The broken line refers to the lattice-dynamical calculation of Dolling, Cowley & Woods (1965). For clarity, the error bars at each temperature are drawn off-vertical.

by Dolling, Cowley & Woods (1965), using the formula

$$B_\kappa = \frac{2\pi}{3}\frac{\hbar}{N_c M_\kappa}\sum_{\mathbf{q}j\alpha}\frac{|e_\alpha(\kappa,\mathbf{q}j)|^2}{\nu_j(q)} \times \left(1 + \frac{2}{\exp\left(\frac{h\nu_j(\mathbf{q})}{k_B T}\right) - 1}\right). \quad (6)$$

The summation in (6) is over the normal modes of vibration ($\mathbf{q}j$) and over the α displacements, where $\alpha \equiv x,y,z$. ν is the frequency of the mode, $\mathbf{q}$ its wavevector and j the polarization index. κ refers to the type of ion: U or O. M_κ is the mass of the ion, $e_\alpha(\kappa,\mathbf{q}j)$ is the α displacement of the κth ion in the normalized eigenvector for the ($\mathbf{q}j$) mode, and N_c is the number of unit cells per unit volume. The frequencies $\nu_j(\mathbf{q})$ and displacements $e_\alpha(\kappa,\mathbf{q}j)$ were determined by Dolling *et al.* by fitting their phonon dispersion curves, measured at room temperature, to those calculated for a shell model of the interionic forces. At high temperatures, above the Debye temperature $\theta_D(\simeq 400$ K for UO_2), we can write $h\nu_j(\mathbf{q}) \ll k_B T$ and the factor in parentheses in (6) becomes

$$2\,k_B\,T/h\nu_j(\mathbf{q}).$$

In the harmonic approximation, the frequencies are independent of temperature, and so B_κ is proportional to T for $T > \Theta_D$. This linear relationship is shown by the broken lines in Figs. 1 and 2.

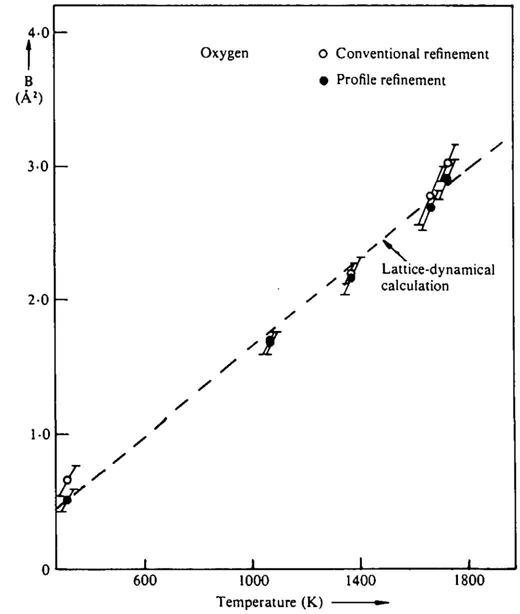

Fig. 2. Temperature dependence of the B values of O, as determined by the two refinement methods. The broken line refers to the lattice-dynamical calculation of Dolling, Cowley & Woods (1965). For clarity, the error bars at each temperature are plotted off-vertical.

4. Profile refinement

The same set of observations was then analysed by the Rietveld method. Each observation y_i of the background-corrected intensity at the scattering angle $2\theta_i$ was assigned a weight

$$w_i = \frac{1}{Y_i + B_i}, \quad (7)$$

where B_i is the background and Y_i $(= y_i + B_i)$ is the total intensity. B_i was estimated by interpolation between regions with no Bragg intensity. The number of observations y_i was restricted to cover the same range of θ_i's as was used in the conventional refinement, § 3. The computer program used for the profile refinement has been described by Hewat (1973), and was modified later by one of the present authors (MWT).

The refinement yielded the three structural parameters (s, B_U, B_O), four instrumental parameters and the lattice parameter a_o. The four instrumental parameters are U, V, W, governing the θ-dependence of the half-width of the reflections (Rietveld, 1969), and the zero-2θ position of the diffractometer. Table 2 lists the structural parameters and the lattice parameter, with their e.s.d.'s. Also given are: the number of experimental points N_P, separated by 0·1° in 2θ, at which the profile was sampled; the quantity

$$R(wI) = \left[\frac{\sum_i w_i[y_i(\text{obs.}) - sy_i(\text{calc.})]^2}{\sum_i w_i[y_i(\text{obs.})]^2}\right]^{1/2};$$

and the agreement factor A_P defined by

$$A_P^2 = \frac{\sum_i w_i[y_i(\text{obs.}) - sy_i(\text{calc.})]^2}{N_P - P_P - P_S}, \quad (8)$$

where P_P $(= 5)$ is the number of profile parameters (*i.e.* U, V, W, zero-2θ and a_o), and P_S is the number of structural parameters.

The B values from Table 2 are included (as closed circles) in the temperature plots in Figs. 1 and 2. At

Table 2. *Results given by the profile-refinement method*

Temperature (K)	B_U (Å²)	B_O (Å²)	s (relative)	N_P	$R(wI)$ (%)	A_P	a_o (Å)
293	0·12	0·51	1·00	99	8·27	3·07	5·4710
	(6)	(7)	(2)				(2)
1073	0·84	1·70	0·95	105	8·54	2·47	5·5135
	(7)	(9)	(1)				(3)
1373	1·31	2·19	0·96	107	9·33	2·51	5·5333
	(9)	(11)	(1)				(3)
1673	1·59	2·70	0·93	93	10·53	2·85	5·5538
	(11)	(15)	(2)				(4)
1733	1·67	2·92	0·92	89	9·26	2·48	5·5580
	(10)	(14)	(2)				(4)

each temperature there is close agreement, to within one e.s.d., of the values derived by the conventional and Rietveld methods of analysis. In principle, the structural parameters given by the two treatments are not identical (Sakata & Cooper, 1979), but in the present case they do not differ significantly.

Using the method of least squares, we have fitted a quadratic curve

$$B(T) = a + bT + cT^2$$

to the experimental points in Figs. 1 and 2. The points were weighted according to their e.s.d.'s. If T is the absolute temperature, the a coefficient is zero for $T > \Theta_D$ and the B factors are then:

$$B_{\rm U} = 8\pi^2\overline{u_{\rm U}^2} = 5{\cdot}958 \times 10^{-4}\,T + 2{\cdot}472 \times 10^{-7}\,T^2$$

and

$$B_{\rm O} = 8\pi^2\overline{u_{\rm O}^2} = 1{\cdot}518 \times 10^{-3}\,T + 7{\cdot}794 \times 10^{-8}\,T^2,$$

where B is in Å^2 and T in K. The positive values of the c coefficients indicate that the thermal amplitudes of the U and O atoms increase more rapidly with temperature than the harmonic lattice-dynamical theory predicts.

The ratio of $(\sigma_i)_P$, the e.s.d. of the ith parameter as determined by the Rietveld method, to $(\sigma_i)_I$, the corresponding quantity for the conventional treatment, is given by:

$$\frac{(\sigma_i^2)_P}{(\sigma_i^2)_I} = \frac{(A_{ii}^{-1})_P}{(A_{ii}^{-1})_I}\,\frac{A_P^2}{A_B^2}, \tag{9}$$

where A_{ii}^{-1} is the diagonal element of the inverse normal matrix corresponding to the ith parameter. Sakata & Cooper (1979) have shown that the value of $(A_{ii}^{-1})_P/(A_{ii}^{-1})_I$ can be estimated from the approximate expression

$$\frac{(A_{ii}^{-1})_P}{(A_{ii}^{-1})_I} \simeq \frac{1}{\varepsilon'}, \tag{10}$$

where the factor ε' is determined by the weights given to the observations in the two methods of refinement.

The e.s.d. ratios predicted by (9) and (10) are reported in column 6 of Table 3, using the agreement factors of Tables 1 and 2. ε' was taken as 1·5, as none of the individual estimates of ε' differed from 1·5 by more than 10%. Columns 2 to 5 in Table 3 list the e.s.d.'s given by the two methods of analysis, and the ratios of these are given in columns 7 and 8. The ratio in column 6 is in reasonable agreement with those in the last two columns. We conclude that the Sakata & Cooper theory accounts satisfactorily for the differences in the e.s.d.'s of the structural parameters obtained by the two methods of analysis.

Table 3. *E.s.d. ratios for profile and conventional refinements*

	$(\sigma_i)_P$: profile		$(\sigma_i)_I$: conventional			$(\sigma_i)_P/(\sigma_i)_I$	
Temperature (K)	$i = B_{\rm U}$ (Å^2)	$i = B_{\rm O}$ (Å^2)	$i = B_{\rm U}$ (Å^2)	$i = B_{\rm O}$ (Å^2)	$\frac{1}{\sqrt{\varepsilon'}}\,\frac{A_P}{A_B}$	$B_{\rm U}$	$B_{\rm O}$
293	0·062	0·072	0·102	0·120	0·59	0·61	0·60
1073	0·071	0·091	0·074	0·090	1·01	0·96	1·01
1373	0·086	0·107	0·052	0·061	1·87	1·65	1·75
1673	0·113	0·145	0·166	0·211	0·71	0·68	0·69
1733	0·104	0·137	0·104	0·138	1·04	1·00	0·99

It is well known that the thermal parameters are much more difficult to measure accurately in a diffraction experiment than the positional parameters. Powder diffraction methods, in particular, tend to give unreliable values for the thermal parameters, because of the difficulty of establishing the background level which can be strongly correlated with the temperature factors. However, the present study has confirmed that the thermal parameters for UO_2, derived from either the profile or integrated-intensity method, are in fairly close agreement with one another over the temperature range 293–1733 K, and with those calculated by lattice dynamics. It appears that the limited peak overlap in the UO_2 data results in a more confident estimate of the background level and a better determination of the temperature factors.

The lattice parameters quoted in Table 2 have been fitted by least squares to a quadratic expression in the temperature T, giving

$$a_o(T) = 5{\cdot}4576 + 4{\cdot}326 \times 10^{-5}\,T + 8{\cdot}477 \times 10^{-9}\,T^2, \tag{11}$$

where a_o is in Å and T in K. The present measurements of a_o extend to higher temperatures than those given previously (*e.g.* Gronvold, 1955).

5. Conclusions

Sakata & Cooper (1979) have analysed several sets of powder diffraction data obtained with neutrons, and have found that for most of these the e.s.d.'s were underestimated by the Rietveld procedure by a factor of at least two. However, the present results demonstrate that this factor is not necessarily as large as this and may vary over quite a large range. Indeed, in two of the five data sets (1073 and 1733 K) the e.s.d.'s given by the conventional and Rietveld refinements are about the same, and in one data set (1373 K) the Rietveld method leads to e.s.d.'s which exceed those from the conventional refinement by a factor of nearly two.

However, the differences between the e.s.d.'s obtained at each of the five temperatures for the two types of refinement can be accounted for satisfactorily by the analysis of Sakata & Cooper. The agreement factor A_B [see (5)] in the conventional refinement reflects the degree of matching between the observed and calculated integrated intensities, whereas the agreement factor A_P [see (8)] for the Rietveld refinement reflects not only the degree of matching between integrated intensities but also that between the shape functions describing the profile of the individual reflections. The structural parameters are determined by the integrated intensities and the profile parameters by the shape functions: it is not surprising that the e.s.d.'s from the Rietveld refinement are different from those from the conventional refinement.

References

BACON, G. E. (1976). *Neutron Diffraction*, 3rd ed. Oxford Univ. Press.

BUSING, W. R., MARTIN, K. O., LEVY, H. A., ELLISON, R., HAMILTON, W. C., IBERS, J. A., JOHNSON, C. K. & THIESSEN, W. E. (1971). *ORXFLS* 3. Oak Ridge National Laboratory, Tennessee.

COOPER, M. J. & SAKATA, M. (1979). *Z. Kristallogr.* **149**, 337–338.

DOLLING, G., COWLEY, R. A. & WOODS, A. D. B. (1965). *Can. J. Phys.* **43**, 1397–1413.

GRONVOLD, F. (1955). *J. Inorg. Nucl. Chem.* **1**, 357–370.

HEWAT, A. W. (1973). Report RRL/73/187. AERE Harwell, Oxfordshire, England.

MALMROS, G. & THOMAS, J. O. (1977). *J. Appl. Cryst.* **10**, 7–11.

RIETVELD, H. M. (1967). *Acta Cryst.* **22**, 151–152.

RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

ROUSE, K. D., WILLIS, B. T. M. & PRYOR, A. W. (1968). *Acta Cryst.* B**24**, 117–122.

SAKATA, M. & COOPER, M. J. (1979). *J. Appl. Cryst.* **12**, 554–563.

YOUNG, R. A., MACKIE, P. E. & VON DREELE, R. B. (1977). *J. Appl. Cryst.* **10**, 262–269.

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The Diffraction Aspect and a Structural Model of Mullite, $Al(Al_{1+2x}Si_{1-2x})O_{5-x}$

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Abstract

Diffraction patterns of various specimens of mullite were recorded using a high-power X-ray generator. The patterns consist of main reflections based on the primitive orthorhombic lattice with $a = 7{\cdot}6$, $b = 7{\cdot}7$ and $c = 2{\cdot}9$ Å, and two types of subsidiary reflections. Although the patterns show no periodicity in reciprocal space, a periodic unitary intensity distribution is deduced using information from the average structure. The distribution of the sites of the removed oxygen atoms in the sillimanite-like ideal structure is obtained from the qualitative values of the unitary intensity. In order to compare the calculated value to the observed continuous intensity distribution in reciprocal space, a structural model was constructed. It contains four sorts of equivalent domains; each domain consists of about 40 000 atoms. These atoms are situated at definite positions in real space, and no partly occupied sites are specified in these models.

Introduction

Mullite, $Al(Al_{1+2x}Si_{1-2x})O_{5-x}$, is a typical non-stoichiometric compound, which ranges in composition from $3Al_2O_3.2SiO_2$ to $2Al_2O_3.SiO_2$. Although its X-ray diffraction patterns are very similar to those of sillimanite, mullite commonly shows diffuse scattering, as pointed out by Taylor (1928), and sometimes shows superlattice reflections as described by Agrell & Smith (1960).

Sadanaga, Tokonami & Takéuchi (1962) determined the average structure of mullite and clarified the structural relationship between mullite and sillimanite. Durovic (1962) independently analyzed the average structure. The results obtained by Sadanaga, Tokonami & Takéuchi (1962) were confirmed by Burnham (1964). It should be noted that Warren (1933) proposed the exact scheme for the mullite structure prior to the above authors.

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