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ON THE USE OF A MODIFIED RADIAL DISTRIBUTION ANALYSIS FOR INDEXING POWDER PATTERNS

by

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Abstract

A modification of the theory of X-ray radial distribution analysis is presented. This modification can serve as a guide to the values of the unit cell dimensions and may be useful in indexing powder patterns of unknown structures, although the use of trial and error methods is not eliminated. This technique is shown to give consistent results with known structures and is applied to the indexing of powder patterns of Pu_3Ru and Pu_5Ru_3 . The powder pattern of Pu_3Ru can be indexed on the basis of an orthorhombic unit cell with $a_0 = 6.216 \text{ \AA}$, $b_0 = 6.924 \text{ \AA}$ and $c_0 = 8.093 \text{ \AA}$, and Pu_5Ru_3 on the basis of a tetragonal unit cell with $a_0 = 8.092 \text{ \AA}$ and $c_0 = 10.023 \text{ \AA}$.

Introduction

The problem of indexing the powder pattern of an unknown structure, which is trivial in the case of cubic symmetry, becomes increasingly difficult as the symmetry is lowered. Many methods, both graphic and analytic, for indexing

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powder patterns have been presented (for examples see ref. 1 and 2). These are all basically trial and error methods. Therefore, any device which can give any information as to distances in the real or reciprocal lattice would be a useful tool which could be used to assist in the indexing of a powder pattern.

Radial Distribution Analysis

The theory for X-ray radial distribution analysis of diffraction data consisting of discrete peaks has been presented by Glusker and Miller⁽³⁾. From their theory:

$$4\pi r^2 \sum_M K_M [g'_M(r) - g_0] = (2r/\pi) (\sum_M Z_M^2) \left\{ \sum_j F_j A_j [\exp(-B's_j^2)] \sin s_j r - (1/4) r \sqrt{\pi} (B+B')^{3/2} \exp[-(1/4) r^2 / (B+B')] \right\} \dots (1)$$

In equation (1), K_M is the effective weighting factor for the M^{th} atom and is approximately equal to Z_M , the atomic number, $g'_M(r)$ is the electron density function, g_0 is the average electron density, A_j is the observed intensity for the j^{th} Bragg peak, F_j is the factor necessary to place the A_j on an absolute basis, $s_j = (4\pi \sin \theta_j) / \lambda = 2\pi / d_j$, and B is the temperature factor coefficient. The factor $\exp(-B's_j^2)$ is a convergence factor introduced in order to decrease spurious detail in the calculated radial distribution function which would be caused by the fact that data exist only to a finite value of s ⁽⁴⁾. The value of B' is usually chosen such that $\exp(-B's_{j \text{ max}}^2) = 1/10$. The presence of a peak in the radial distribution function at $r = r_1$ indicates that more than the average amount of electron density is associated with atoms that have separations at this value.

The radial distribution function calculated according to equation (1) from the powder pattern of a given structure will have peaks at values of r equal to the unit cell dimensions. However, these will generally be unidentifiable in the maze of peaks due to all other interatomic distances.

Consider a hypothetical structure which has the identical unit cell as the unknown structure whose powder pattern is to be indexed, but has only one atom per unit cell. The powder pattern of this hypothetical structure will have lines, all with the same structure factor, at the identical positions as the unknown structure (including lines corresponding to unobserved reflections from the unknown structure). The radial distribution function calculated for this hypothetical structure would therefore have peaks at values of r equal only to distances in the real lattice of the unknown structure and should be of value for indexing the powder pattern of the unknown structure.

If it is assumed that $F_j A_j = 1$ for all observed reflections, then the radial distribution function for this hypothetical structure can be calculated from the powder pattern of the unknown structure by equation (2).

$$r \sum_M K_M [g'_M(r) - g_0] \propto r D(r) \propto \sum_j [\exp(-B's_j^2)] \sin 2\pi(r/d_j) \dots \dots \dots (2)$$

This $rD(r)$ vs. r curve will be an approximation and will not be proportional to the exact radial distribution function for the hypothetical structure because multiplicity has not been taken into account and because reflections which are unobserved for the unknown structure cannot be included. This latter factor may cause several peaks, due to interatomic distances not corresponding to lattice translations, to persist. Neglect of the term,

$(1/4)r \sqrt{\pi(B + B')}^{-3/2} \exp[-(1/4)r^2/(B + B')]$, will result in a strong peak near

the origin, where there can be no interatomic distances, and will not appreciably affect the curve for larger values of r . Equation (2), in addition to suppressing the peaks not corresponding to lattice translations, has the additional advantage over equation (1) that careful, laborious determination of the factors F_j and the intensities A_j are not required.

Application to Known Structures

As a preliminary check of the applicability of this method it has been applied to known structures. The $rD(r)$ vs. r curves calculated from the powder patterns of Sb and α -U, for the hypothetical unit cell, are shown in Figs. 1 and 2, respectively. The unit cell of Sb is rhombohedral with $a_0 = 4.4976$ kX (4.507 Å) and $\alpha = 57^\circ 6' 27''$,⁽⁵⁾. The unit cell of α -U is orthorhombic with $a_0 = 2.854$ Å, $b_0 = 5.869$ Å and $c_0 = 4.955$ Å⁽⁶⁾. Vertical lines are drawn under the curves to indicate the values of the known distances in the real lattice as well as several other interatomic distances. In both cases the agreement between the theoretical predictions and experimental data is pleasing.

Application to Unknown Structures, a. Pu_3Ru

As a final test of the applicability of this method it has been applied to the indexing of the powder patterns of unknown structures. A melt of Pu_3Ru containing 12.34 wt % Ru (calc. for Pu_3Ru , 12.36 wt % Ru) was prepared, annealed at 540°C for 35 days and powdered. Debye-Scherrer patterns were made with CuK_α radiation ($\lambda = 1.5418$ Å). Attempts at indexing this pattern by the standard methods^(1,2) were unsuccessful.

The $rD(r)$ vs. r curve for the hypothetical unit cell is shown in Fig. 3 and has strong peaks at 3.3 Å and 6.6 Å, a minor peak at 5.3 Å and a broad peak between 8.4 Å and 9.2 Å. The assumption of the existence of distances in the

real lattice near 3.3 Å or 5.3 Å did not lead to successful indexing. However, when the existence of distances near 6.6 Å and 8.4 Å was assumed, it was possible to index the powder pattern on the basis of an orthorhombic unit cell. The lattice constants, refined by least squares, are $a_0 = 6.216$ Å, $b_0 = 6.924$ Å, $c_0 = 8.093$ Å, all $\sigma = 0.001$ Å. (These values are illustrated by the vertical lines on Fig. 3 to show the agreement obtained.) The density, calculated for $Z = 4$, is 15.60 g/cm³ (observed, 15.50 g/cm³). The agreement between observed and calculated values of $Q (= 4\sin^2\theta/\lambda^2)$ is shown in Table I. The lack of any systematic absences suggests that the space group, if centrosymmetric, is Pmmm. The strong peak at 3.3 Å probably corresponds to Pu-Pu distances. This value is approximately twice the metallic radius of Pu, 1.58 Å⁽⁷⁾.

b. Pu₅Ru₃

A melt of Pu₅Ru₃ containing 20.21 wt % Ru (calc. for Pu₅Ru₃, 20.24 wt % Ru) was prepared and annealed at 860°C for 11 days. The $rD(r)$ vs. r curve for the hypothetical unit cell is shown in Fig. 4. Peaks are observed at 3.55 Å, 5.4 Å, 6.5 Å, 8.05 Å, 10.0 Å, 11.4 Å and 12.8 Å. The powder pattern could not be indexed with the assumption of the existence of distances in the unit cell equal to any of the first three values. Since the first two peaks correspond to similar peaks for Pu₃Ru, it does not seem unreasonable to assume that these peaks also represent Pu-Pu or Pu-Ru interactions not corresponding to lattice translations. The observation that $11.4 \approx 8.05\sqrt{2}$ and $12.8^2 \approx 10.0^2 + 8.05^2$ enabled the first 25 lines of the pattern to be indexed* on the basis of a tetragonal unit cell with $a_0 = 8.092$ Å and $c_0 = 10.023$ Å. (These values are

* The remainder of the pattern cannot be unambiguously indexed because of the large size of the unit cell.

illustrated by the vertical lines on Fig. 4.) The density, calculated for $Z = 4$, is 15.17 g/cm^3 (observed, 14.82 g/cm^3)*. The space group, if centrosymmetric, is probably $P4/mmm$. The agreement between the observed and calculated values of Q is shown in Table II.

Conclusions

A modification of the theory of X-ray radial distribution analysis has been presented in order to make this technique applicable to the problem of indexing the powder pattern of an unknown structure. Although the use of trial and error methods for indexing powder patterns is not eliminated, the modified radial distribution curve calculated from the powder pattern of an unknown structure can serve as a valuable guide to the values of the unit cell dimensions. The modified theory has given consistent results when applied to known structures and has been used successfully to index powder patterns of Pu_3Ru and Pu_5Ru_3 after standard methods had failed.

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* A plot of reciprocal density vs. composition for the phases Pu_3Ru , PuRu , $\text{PuRu}_2^{(8)}$ and Ru suggests that the value 14.82 g/cm^3 may be too low. A value of 15.20 g/cm^3 lies on the straight line determined by the other four densities.

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Figure Captions

Figure 1. The $rD(r)$ vs. r curve for the hypothetical unit cell of Sb.

Figure 2. The $rD(R)$ vs. r curve for the hypothetical unit cell of α -U.

Figure 3. The $rD(r)$ vs. r curve for the hypothetical unit cell of Pu_3Ru .

Figure 4. The $rD(r)$ vs. r curve for the hypothetical unit cell of Pu_5Ru_3 .

Table I. Observed and Calculated Values of Q for Pu₃Ru

Q _{obs}	Int.	hkl	Q _{calc}
0.0341	vvw	011	0.0362
0.0863	vvw	102	0.0870
0.1045	w	200	0.1035
0.1113	vw	120	0.1093
0.1178	vw	201	0.1188
0.1230	w	210	0.1244
0.1259	vw	121	0.1246
0.1359	s	003	0.1374
0.1415	s	211	0.1397
0.1446	ms	022	0.1445
0.1572	w	013	0.1583
0.1607	m	103	0.1633
0.1678	vs	122	0.1703
0.1896	s	030	0.1877
		221	0.2022
0.206*	m	031	0.2030
		130	0.2136
		131	0.2289
0.2309	vw	300	0.2329
		032	0.2488
0.2511	vw	310	0.2538
0.2668	vw	014	0.2652
0.3262	s	033	0.3251
		024	0.3277
0.3332	vw	040	0.3338
		133	0.3510
0.352*	vvw	232	0.3523
		124	0.3536

Q _{obs}	Int.	hkl	Q _{calc}
0.3778	w	322	0.3774
0.3837	ms	005	0.3817
0.3966	m	042	0.3949
0.4097	m	105	0.4076
0.4145	s	400	0.4141
		330	0.4206
0.4228	vvw	142	0.4208
		410	0.4350
0.4351	vw	331	0.4359
0.4497	m	411	0.4503
0.4590	w	134	0.4579
0.4776	vvw	304	0.4772
		412	0.4961
		143	0.4971
0.4973	m	420	0.4975
		314	0.4981
		242	0.4984
0.5205	ms	050	0.5215
0.5378	vvw	051	0.5368
0.5466	mw	150	0.5473
		016	0.5705
0.5717	m	413	0.5724
0.6097	s	152	0.6085
		342	0.6278
0.6302	mw	026	0.6330
0.6382	m	251	0.6403
0.6540	mw	206	0.6531

* Extremely broad feature.

A total of 137 reflections with Q < 0.658 are possible.

Table II. Observed and Calculated Values of Q for Pu_5Ru_3

Q_{obs}	Int.	hkl	Q_{calc}
0.0248	vw	101	0.0253
0.0299	vw	110	0.0305
0.0746	vw	210	0.0764
0.0877	w	{ 211	0.0864
		{ 003	0.0896
		{ 202	0.1009
0.1029	vw	{ 103	0.1047
0.1203	m	113	0.1201
0.1242	w	220	0.1222
0.1374	vw	300	0.1374
0.1436	s	301	0.1474
0.1551	ms	310	0.1527
0.1583	vw	004	0.1593
0.1648	w	{ 222	0.1620
		{ 311	0.1627
		{ 213	0.1660
0.1741	s	104	0.1746
0.1784	vs	302	0.1772
0.1894	m	114	0.1898
0.2592	w	410	0.2596
0.2818	mw	224	0.2815
0.3277	vw	215	0.3253
0.3464	ms	422	0.3452
0.3806	ms	430, 500	0.3818
0.3855	w	305	0.3863
0.3971	w	510	0.3971
0.4143 } *	ms	{ 414	0.4189
		{ 206	0.4195
		{ 432, 502	0.4216
0.4200 }		{ 334	0.4342
0.4329	vs	{ 216	0.4348

* Broad line, not completely resolvable.

A total of 81 reflections with $Q < 0.435$ are possible.

Figure 1. The $rD(r)$ vs. r curve for the hypothetical unit cell of Sb.

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Figure 2. The $rD(r)$ vs. r curve for the hypothetical unit cell of α -U.

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Figure 3. The $rD(r)$ vs. r curve for the hypothetical unit cell of Pu_3Ru .

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Figure 4. The $rD(r)$ vs. r curve for the hypothetical unit cell of Pu_5Ru_3 .

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