research papers

ZONES: a search/match database for single-crystal electron diffraction

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ZONES is a relational database built from NIST Crystal Data for the identification of single crystals by selected area electron diffraction (SAED) and elemental analysis using Microsoft *Access 97* for the personal computer (subsequently converted to *Access 2000*). The two largest experimental d spacings and included angle in a zone are matched against values calculated from reduced unit cells, thereby fully and rigorously incorporating the effects of double diffraction. A total of 79 136 inorganic phases are included with original Crystal Data reference codes, allowing access to all the information in NIST Crystal Data. Specific examples illustrate the robustness of this approach. This database will be most useful to researchers in mineralogy, metallurgy, materials science, forensics and analytical chemistry who seek to identify well characterized phases with known unit cells.

1. Introduction

This paper concerns the identification of a crystalline phase from a single (0-level) zone-axis 'photograph' (or digital equivalent), obtained in SAED mode, and elemental analysis, such as that obtained by energy dispersive (X-ray) spectrometry (EDS). The problem has been reduced to that of matching three numbers from the pattern, d_1, d_2 and φ, with calculated values in a database of known materials (Andrews *et al.*, 1971; Lally & Lee, 1977, 1978). These three parameters are defined as the two maximum d spacings in the zone (d_1, which is the largest, and d_2, the next largest), and their interplanar angle, φ. Indexing the photograph is unnecessary and is not an identification tool. On the other hand, others (Carr *et al.*, 1986, 1987, 1989) have found that for a polycrystalline electron diffraction database, inclusion of elemental information is necessary to limit the possible solutions to a manageable number. This premise is also adopted here.

Search/match procedures for polycrystalline electron diffraction have been reviewed previously (Anderson *et al.*, 1993; Mighell & Karen, 1996). If a full unit cell can be determined, the National Institute for Standards and Technology (NIST) Crystal Data (Stalick & Mighell, 1986) can be searched directly (Karen & Mighell, 1992; Karen & Mighell, 1993) with the reduced unit-cell parameters. The same applies to a single crystal if a unit cell can be determined, *e.g.* through convergent-beam electron diffraction (CBED). However, other X-ray diffraction databases, such as the Powder Diffraction File (PDF) or a special sorting thereof, the EISI, Elemental and Interplanar Spacing Index (Mighell *et al.*, 1988), are not useful for zone-axis photographs because of the lack of angular data (φ) and the lack of data obtained solely from double diffraction (Denley & Hart, 2002).

ZONES contains up to 25 zones (calculated d_1, d_2, φ) per phase plus coded elemental analyses above $Z = 10$. It has been successful in identifying a wide variety of phases from zone-axis SAED and EDS data. Successful searches employed test data obtained experimentally and from the literature, with errors of up to 4% in d and 2° in φ. The entire class of 'inorganic' phases in NIST Crystal Data (Version J, 1997) was incorporated (79 136 phases in all).

2. Construction of the database – ZONES

2.1. Loading NIST Crystal Data into Microsoft *Access 97*

NIST Crystal Data (Release J, 1997) is a large formatted ASCII file of crystallographic, chemical and physical data (Stalick & Mighell, 1986; Mighell & Karen, 1996) for 237 660 phases, of which 79 136 are inorganic phases considered suitable for identification by electron diffraction. Loading its 16 record types into relational database tables in Microsoft *Access 97* has been described recently (Hart & Denley, 2002). Data fields in these records provided extremely useful supplementary information for candidate phases identified through ZONES searches. Additionally, combined queries involving diffraction data and other data in Crystal Data can be customized through *Access 97*.

The database ZONES contains three permanent tables, described below. Searches are performed through a macro, macZones, which consists of several queries, some resulting intermediate tables, and one output report.

2.2. ZONES tables

The first table contains records with five fields: (i) the unique crystal data reference code field (herein after called

Table 1
Stored zones.

Indices are based on the reduced unit cell.

Zone number	U,V,W	d_1 $h_1k_1l_1$	d_2 h_2,k_2,l_2
1	0,0,1	1,0,0	0,1,0
2	0,1,0	1,0,0	0,0,1
3	1,0,0	0,1,0	0,0,1
4	0,1,−1	1,0,0	0,1,1
5	1,0,−1	0,1,0	1,0,1
6	1,−1,0	0,0,1	1,1,0
7	0,1,1	1,0,0	0,1,−1
8	1,0,1	0,1,0	1,0,−1
9	1,1,0	0,0,1	1,−1,0
10	−1,1,1	1,1,0	1,0,1
11	1,−1,1	1,1,0	0,1,1
12	1,1,−1	1,0,1	0,1,1
13	−1,1,2	1,1,0	1,−1,1
14	1,−1,2	1,1,0	1,−1,−1
15	−1,2,1	1,0,1	1,1,−1
16	1,2,−1	1,0,1	1,−1,−1
17	2,1,−1	0,1,1	1,−1,1
18	2,−1,1	0,1,1	1,1,−1
19	1,1,1	1,−1,0	1,0,−1
20	1,1,−2	1,−1,0	1,1,1
21	1,1,2	1,−1,0	1,1,−1
22	1,−2,1	1,0,−1	1,1,1
23	1,2,1	1,0,−1	1,−1,1
24	−2,1,1	0,1,−1	1,1,1
25	2,1,1	0,1,−1	1,−1,−1

CODE, designated 'keycode' in the database), (ii) a zone number, (iii) d_1, (iv) d_2, and (v) φ. For each phase there is one record for each zone $[U,V,W]$ (Table 1). These are the most prominent zones, *i.e.* those with highest reciprocal-lattice density. Redundancies caused by metric reduced unit-cell symmetry are deleted. Crystal orientation can be determined by the zone number and Table 1 (not necessary for identification). The parameters d_1, d_2 and φ are calculated from reduced unit-cell parameters from NIST Crystal Data using equations for a triclinic unit cell from Kasper & Lonsdale (1972) and are stored as integers: $100d_1$, $100d_2$, 10φ.

The second database table consists of one record with four fields per phase: CODE, FORMULA, M (for mineral), A (for alloy), exactly as described for the RINGS database by Denley & Hart (2002). FORMULA is the chemical formula field from NIST Crystal Data.

The third database table consists of binary-coded elemental information for each phase, exactly as described for the RINGS database (Denley & Hart, 2002).

Data for each phase are linked together in the three tables by the unique keycode, CODE, from NIST Crystal Data. The CODE also allows access to the other data in NIST Crystal Data.

3. Input/output

3.1. Input

The following input dialogs request information from the user.

Input box 1. Enter the symbol of an element known to be present ($Z > 10$). Repeat for each heavy element. No unspe-

cified heavy elements will be allowed in the solution, and all specified elements must be present. This implies that a complete X-ray (or other comparable elemental) analysis is available. Enter '0' (zero) to stop adding elements. All elements with $Z \leq 10$ cannot be entered and are considered to be possibly present (*i.e.* any combination of these light elements, including none, is allowed).

Input box 2a. Enter d_1, the largest d spacing of the zone, in Å.

Input box 2b. Enter d_2, the second largest d spacing of the zone, in Å.

Input box 2c. Enter φ, the acute angle between $\mathbf{d}_1^*$ and $\mathbf{d}_2^*$ in degrees.

Input box 3a. Enter the experimental error limit on d spacing, δd, in % (recommended input 1.5). A match occurs when a database d spacing (d_1 and d_2) is within this percent of the experimental value, *i.e.* when

$$(100 - \delta d)d(\text{exp.}) \leq [100d(\text{database})] \leq (100 + \delta d)d(\text{exp.}). \tag{1}$$

Input box 3b. Enter the experimental error limit on φ, $\delta\varphi$, in degrees (recommended input 1.0). A match occurs when

$$10[\varphi(\text{exp.}) - \delta\varphi] \leq [10\varphi(\text{database})] \leq 10[\varphi(\text{exp.}) + \delta\varphi]. \tag{2}$$

3.2. Output

A report, rptZones, is opened automatically by the macro macZones. Potential solutions are listed as: CODE, FORMULA, d_1, d_2, φ. Common materials have multiple listings from different experimental sources. Isomorphs and solid solutions may also appear. There can be some incorrect solutions by coincidence, but these are relatively rare and stand out among the more likely solutions.

In the following examples all searches were of the entire database of 79136 phase entries. No other information was used, such as mineral, alloy, *etc.*

4. Results and discussion

4.1. Fluorite

Table 2 shows output for data from fluorite, CaF_2, as measured on film: $d_1 = 3.19$ Å, $d_2 = 3.18$ Å, $\varphi = 70.2°$. All phases are correct except one (Ca), which has the poorest d matches.

4.2. Molybdite

Molybdite, MoO_3, is a TEM standard used to calibrate the rotational effect in going from transmission mode to diffraction mode. A common diffraction pattern has $d_1 = 3.96$ Å, $d_2 = 3.70$ Å, $\varphi = 90.0°$. These d spacings are produced by double diffraction and are absent on the PDF card for MoO_3. Table 3 gives the results of the ZONES search: six MoO_3 phases were found.

Table 2
Fluorite.

$d_1 = 3.19$ Å, $d_2 = 3.17$ Å, $\varphi = 70.2°$, $\delta d = 1.5\%$, $\delta\varphi = 1°$. Element: Ca.

CODE	Formula	d_1 (Å)	d_2 (Å)	φ (°)
022526	CaF_2	3.15	3.15	70.5
037401	Ca	3.22	3.22	70.5
121858	CaF_2	3.15	3.15	70.5
713957	CaF_2	3.15	3.15	70.5
F901289	CaF_2	3.15	3.15	70.5
F902585	CaF_2	3.15	3.15	70.5

Table 3
Molybdite.

Common zone: $d_1 = 3.96$, $d_2 = 3.70$, $\varphi = 90.0°$, $\delta d = 1.5\%$, $\delta\varphi = 10°$. Element: Mo.

CODE	Formula	d_1 (Å)	d_2 (Å)	φ (°)
003676	MoO_3	3.96	3.69	90
023201	MoO_3	3.93	3.67	90
027566	MoO_3	3.95	3.69	90
713757	MoO_3	3.96	3.69	90
F902107	MoO_3	3.96	3.69	90
F941944	MoO_3	3.93	3.69	90

Table 4
Hornblende.

$d_1 = 18.00$, $d_2 = 9.57$, $\varphi = 90.0°$, $\delta d = 1.5\%$, $\delta\varphi = 10°$. Elements: Ca, Fe, Mg, Si.

CODE	Formula	d_1 (Å)	d_2 (Å)	φ (°)
036656	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH,F)_2$	18.06	9.50	90
036659	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH,F)_2$	18.09	9.49	90
036667	$Ca_2(Fe,Mg)_5Si_8O_{22}(OH,F)_2$	18.13	9.53	90
036670	$Ca_2(Fe,Mg)_5Si_8O_{22}(OH,F)_2$	18.10	9.53	90
036671	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH,F)_2$	18.08	9.49	90
109098	$Ca_3Fe(Mg,Fe)_4Si_8O_{22}(OH)_2$	18.12	9.52	90

Table 5
Fe_3C.

$d_1 = 5.16$, $d_2 = 4.66$, $\varphi = 90°$, $\delta d = 4\%$, $\delta\varphi = 2°$. Element: Fe.

CODE	Formula	d_1 (Å)	d_2 (Å)	φ (°)
038287	Fe_3C	5.07	4.52	90
038290	Fe_3C	5.08	4.52	90
038291	Fe_3C	5.08	4.52	90
038308	$Fe_3(C,B)$	5.27	4.48	90
712191	Fe_3C	5.09	4.52	90
713913	Fe_3C	5.09	4.52	90

4.3. Hornblende

Table 4 shows output for literature (Booth *et al.*, 1974) experimental data on hornblende, $Ca_2(Mg,Fe)Si_8O_{22}(OH,F)_2$. The pattern was successfully identified with ZONES without the need to index.

4.4. Fe_3C

Table 5 shows output for Fe_3C considered as unknown data for a phase containing Fe (Goehner & Prakask, 1977). The experimental data had large errors of 4% and 2°, yet the correct phase solution was obtained, plus one boron isomorph. Goehner & Prakask (1977) assumed the known structure to index the reflections.

4.5. Search simulations

Table 6 contains results of simulated searches for ten phases, representing all crystal systems, in which input of the maximum d_1/maximum d_2 and the minimum d_1/minimum d_2 zones for the input phase in the database are, respectively, matched against the entire database. Although all input phases were minerals, this fact was not used in the search. The total number of 'hits' and the number of 'correct' hits are listed in each case. Typical common phases like these have multiple database entries from different experimental sources. The large percentage of virtually identical correct hits in each case demonstrates that this search/match scheme is very robust. Many incorrect solutions were closely related solid solutions or isomorphs. Examples of these are: for halite, $Na(Cl,CN)$; for pyrite, FeS and Fe_2S_3; for calcite, CaC_2B_2.

By way of comparison with the procedures of Mighell & Karen (1990), Karen & Mighell (1992, 1993), the reduced unit cell of each phase in the table was searched against NIST Crystal Data (as implemented in §2.1), and the total number of hits and correct hits were entered in the last column of Table 6. Generally similar results were obtained by both search methods, except in crystallographically less well defined cases (albite, kaolinite, and to a lesser extent quartz/SiO_2) where our approach produced more correct hits. Structurally similar phases with different unit cells (especially crystal symmetry) will not always be found in a reduced unit-cell search. Since d spacings are more closely related to structure than unit cells and are often nearly equal among polymorphs and isomorphs, our approach does tend to produce more hits.

Additionally, there is considerable mathematical complexity in determining reduced unit-cell parameters from diffraction data by procedures guaranteed to produce a 'unique', 'conventional' result (considering the possible permutations) for a_r, b_r, c_r, α_r, β_r, γ_r, the reduced unit-cell parameters. It can also be difficult to obtain the required two zone-axis patterns and their interaxial angle from the same crystal in SAED or to interpret a CBED pattern. Matching the three numbers d_1, d_2 and φ is conceptually and practically far simpler than either of these full-unit-cell approaches.

5. Summary and conclusions

ZONES, a database for single-crystal identification based on a zone-axis photograph and elemental analysis, has all the robustness of a reduced-unit-cell search, but requires simpler input and no knowledge of crystallography to use. In certain cases of isomorphism or polymorphism, additional related solutions may reveal structural relationships that are not apparent from unit-cell comparisons alone.

In spite of many literature references focused on indexing of a zone-axis photograph as proof of identification, indexing is unnecessary for routine identifications with ZONES, because all reciprocal-lattice points in a zone are obtained by simple scalar additions of the unit vectors $\mathbf{d}_1^*$ and $\mathbf{d}_2^*$ and add no new information for identification. Indexing of d_1 and d_2 was performed in building the database. Reference to stored

Table 6
Search simulations.

CS = crystal system: A = anorthic (triclinic); M = monoclinic; O = orthorhombic; T = tetragonal; R = rhombohedral; H = hexagonal; C = cubic. The first entry for each phase is the maximum d_1, d_2; the second entry is the minimum d_1, d_2. Error limits: 1.5%, 1°.

CODE	Name	Formula	CS	d_1	d_2	φ	Hits/correct	Hits/correct (reduced cell)
000449	Albite	$Na(Si_3Al)O_8$	A	6.38	6.38	86.4	12/11	6/6
				4.02	3.78	70.6	13/13	
038274	Aragonite	$CaCO_3$	O	7.96	5.73	90.0	7/6	6/6
				3.75	3.39	82.4	6/6	
038065	Calcite	$CaCO_3$	R	5.68	4.19	75.8	9/9	7/7
				2.68	2.49	90.0	10/7	
003505	Gypsum	$CaSO_4.2H_2O$	M	7.58	5.37	69.3	7/7	7/7
				3.55	3.17	86.0	7/7	
033122	Halite	$NaCl$	C	3.25	3.25	70.5	3/3	3/3
				1.99	1.70	90.0	4/3	
001144	Kaolinite	$Al_2(OH)_4Si_2O_5$	A	8.95	7.14	88.1	2/2	2/1
				4.12	3.68	72.4	6/6	
003676	Molybdite	MoO_3	O	13.9	3.96	90.0	5/5	4/4
				2.70	2.65	86.0	5/5	
024148	Pyrite	FeS_2	C	5.41	5.41	90.0	12/10	12/12
				3.83	3.12	90.0	12/10	
026970	Quartz	SiO_2	H	5.40	4.25	90.0	24/23	22/22
				3.34	2.28	71.8	29/29	
807069	Zircon	$ZrSiO_4$	T	4.66	4.66	90.0	17/14	14/14
				2.98	2.64	63.7	14/14	

zone indices and Table 1, plus some simple scalar additions will index the entire zone-axis pattern with respect to the reduced unit cell if required for other studies of crystal orientation or structure.

NIST Crystal Data in relational database form is a powerful supplementary tool for crystal identification, providing extra search or screening criteria and convenient access to other crystallographic data, including references. This has been pointed out previously (Anderson *et al.*, 1993; Mighell & Karen, 1996) in general, but implementation with the use of the common desktop tool, Microsoft *Access 97*, provides additional convenience and flexibility in search/match, data transfer and reporting. Interface to additional common desktop software (spreadsheet and word processing) is built in. For example, Tables 2–5 in this paper were generated easily from the Microsoft *Access 97* search output.

Efforts are underway to make ZONES available commercially, and a patent is pending. It should be a useful tool for microanalysts in other fields, who are not skilled in crystallography.

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