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RINGS: a new search/match database for identification by polycrystalline electron diffraction

David R. Denley* and Haskell V. Hart

Shell Chemical LP, PO Box 1380, Houston, TX 77251-1380, USA. Correspondence e-mail: david.denley@shell.com

RINGS is a relational database built from NIST Crystal Data for the identification of polycrystalline solids by selected area electron diffraction (SAED) and elemental analysis using Microsoft *Access 97* (subsequently converted to *Access 2000*). Experimental *d* spacings 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 advantages over previous approaches to the problem. 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

1.1. Background and purpose

Search/match procedures for polycrystalline electron diffraction have been previously reviewed (Anderson *et al.*, 1993; Mighell & Karen, 1996) and, in the absence of unit-cell determination, the only widely available and comprehensive database is the NIST/Sandia/ICDD Electron Diffraction Database (Carr *et al.*, 1986, 1987, 1989), queried through a program known as *EDSEARCH*. If a unit cell can be determined, the National Institute for Standards and Technology (NIST) Crystal Data (Stalick & Mighell, 1986) can be searched directly (Anderson *et al.*, 1993; Karen & Mighell, 1992, 1993) with the reduced unit-cell parameters. Other approaches are based on the Powder Diffraction File (PDF) or a special sorting thereof called the EISI, Elemental and Interplanar Spacing Index (Mighell *et al.*, 1988).

As noted by previous researchers on this subject, a major disadvantage of using any version of the PDF (which is based on X-ray diffraction) is that some *d* spacings measured by electron diffraction are the result of double diffraction only, and are therefore not observed in X-ray diffraction or included in the PDF. Unfortunately, these *d* spacings, generally among the largest of the electron diffraction patterns, are among the most structurally characteristic, because they are in the region of reciprocal space with the lowest radial density of lattice points, *i.e.* nearest the origin.

Unfortunately, there is no existing comprehensive database for electron diffraction that utilizes *d*-spacing search/match (as opposed to unit-cell searching) and that rigorously incorporates double diffraction. As seen below, rigorous treatment is possible by calculating *d* spacings from reduced unit cells, conveniently available in NIST Crystal Data. In this way, all experimentally observable *d* spacings are contained in the database, and no database *d* spacing is impossible to be observed experimentally (weak intensities not included).

1.2. Double diffraction

Double diffraction is the phenomenon of an apparent reflection from Miller planes ($h_3k_3l_3$) actually resulting from two reflections: the first from planes ($h_1k_1l_1$), followed by a second from planes ($h_2k_2l_2$). The relationships between the three sets of Miller indices are (Andrews *et al.*, 1971):

$$h_3 = h_1 + h_2, \tag{1}$$

$$k_3 = k_1 + k_2, \tag{2}$$

$$l_3 = l_1 + l_2. \tag{3}$$

Or, in reciprocal-lattice vector form:

$$\mathbf{d}_3^* = \mathbf{d}_1^* + \mathbf{d}_2^*. \tag{4}$$

Double-diffraction reflections can superimpose normal single reflections, or they can 'add' normally (X-ray) 'extinct' reflections to an electron diffraction pattern. The latter case must be understood in the context of generating comprehensive *d* spacings in a database for electron diffraction. It remains then to demonstrate which additional double-diffraction *d* spacings must be added to those generated from the full-symmetry unit cell. As an example, it is shown in Table 1 that there are no new general reflections generated by double diffraction for a *C*-centered unit cell. Proof is based on the parity (odd or even) of a Miller index (3) [in equations (1)–(3)], resulting from the sum of indices (1) and (2). Only three parity cases exist:

Case *A*: odd plus even equals odd.
Case *B*: even plus even equals even.
Case *C*: odd plus odd equals even.

Table 1
Double diffraction in *C*-centering ($h + k$ = even).

Parities (odd/even) of double-diffraction reflections in row (3) resulting from single reflections in rows (1) and (2) through the application of equations (1)–(3). No new parity combinations (in **bold**) are generated by double diffraction.

		Reflection/subscript		
		h	k	l
Case *A*				
	(1)	odd	odd	odd or even
	+ (2)	even	even	odd or even
	= (3)	**odd**	**odd**	odd or even
Case *B*				
	(1)	even	even	odd or even
	+ (2)	even	even	odd or even
	= (3)	**even**	**even**	odd or even
Case *C*				
	(1)	odd	odd	odd or even
	+ (2)	odd	odd	odd or oven
	= (3)	**even**	**even**	odd or even

Working through the various index sum parities for symmetry-allowed reflections, $h_1k_1l_1$ and $h_2k_2l_2$, of various classes of reflections (general, zonal or serial), leads to the following principles for determining which additional 'extinct' reflections are allowed by double diffraction:

(i) Extinct reflections due to cell centering (C, F or I) are not added by double diffraction.

(ii) Extinct reflections due to glide planes (axial, diagonal or diamond) are added by double diffraction.

(iii) Extinct reflections due to screw axes are added by double diffraction.

As a result of the foregoing principles (i)–(iii), most importantly:

(iv) Reflections comprehensively generated from a reduced (primitive) unit cell treated as 'triclinic' are all allowed in electron diffraction.

(v) There are no observable reflections not included in (iv) above.

These principles, plus the known fact that indices based on reduced cells generate exactly the same planes as indices based on full-symmetry cells, allow for the generation of a database of *d* spacings for electron diffraction from reduced unit cells and a single comprehensive Miller index generation scheme, without regard for crystal symmetry or space group. The simple triclinic formula is used (Kasper & Lonsdale, 1972) to calculate the *d* spacing from reduced cell parameters and corresponding Miller indices. Hence, NIST Crystal Data, which contains the reduced unit cells, is ideally suited for the generation of an electron diffraction database.

2. Construction of the database – RINGS

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

NIST Crystal Data (Version J, 1997) is a large formatted file of crystallographic, chemical and physical data (Stalick & Mighell, 1986) for 237660 phases, of which 79136 are inorganic phases considered suitable for identification by electron diffraction. Data are organized into 16 record types (1–9 and A–E, J, K) of several or more data fields for each phase. Each record type contains a crystal data reference code field (herein called CODE, designated 'keycode' in the database) unique to each phase. As a preliminary to building a database for electron diffraction, the entire NIST Crystal Data was broken down into separate field-formatted files with Microsoft Visual Basic for Applications. As an additional research tool, the entire Crystal Data was then loaded from these files into 16 Microsoft *Access 97* relational database tables, one for each record type. These provided extremely useful supplementary information for candidate phases identified through the electron diffraction database search. Additionally, combined queries involving diffraction data and other data in Crystal Data were customized through *Access 97*.

The database RINGS contains three permanent tables, described below. Searches are performed through a macro, macRings, which consists of several queries, some resulting intermediate tables, and two output reports.

2.2. *d* spacings

For each inorganic phase, the appropriate reduced unit cell is read from the file of record type D and all *d* spacings greater than 0.8 Å are calculated. Duplicates are removed and the largest 25 (maximum) are sorted, converted to integers as 100*d*, and written to file with the unique phase Crystal Data CODE. This file is read into RINGS as a table, tblICodeRings.

2.3. Chemical formulae

Chemical formulae are contained in record type 7. The appropriate file is read and both the FORMULA and the CODE are extracted and written to a new file, which is read into *Access 97* as a table, tblIFormulas. NIST FORMULAs are copied directly so that in output tables, subscript numerals are represented on-line and water of hydration is preceded by a '!' according to NIST convention (Stalick & Mighell, 1986).

2.4. Elemental analysis

Since elemental analysis is required to solve most identification problems (Carr *et al.*, 1986), a Visual Basic for Applications program identifies the atomic symbols in each FORMULA and encodes them in binary through a series of seven two-byte integers (N_1–N_7) as follows. The elements are placed into seven groups (i = 1–7) by Z: 1–15, 16–30, 31–35, 46–60, 61–75, 76–90, and 91–105. For each element present in a formula, a number is calculated: 2 to the power $Z - 15\,(i - 1)$, where i is the group number (1–7) above. Seven numbers N_i (i = 1–7) are calculated as:

$$N_i = \sum_Z 2^{Z-15(i-1)}, \qquad (5)$$

where the sum is over all elements present in the FORMULA for each group i, without regard to their stoichiometric ratios. An *Access 97* table, tblIElements, is formed from the CODE and N_1–N_7 for each phase. Hence, each unique combination of elements (without regard to stoichiometry) will have a unique set of numbers N_1–N_7. A preliminary search of these numbers

Table 2
NiO results, RINGS tblSummary.

FOM	CODE	Formula	Matching d spacings	d spacings in range	Missing d spacings
10	22186	NiO	11	12	1
10	H727456	NiO	11	12	1
9	024133	NiO	9	9	0
8	022487	NiO	9	10	1
8	700611	NiO	9	10	1
8	804006	NiO	9	10	1
6	021989	NiO	8	10	2
1	I728035	NH_4NiF_3	7	13	6
−3	025859	Ni_2O_3	9	21	12
−5	111370	NiO	8	21	13
−6	F22306	$Ni(HCO_3)_2$	7	20	13
−7	F722364	Li_2NiF_4	7	21	14
−9	024788	NiOOH	7	23	16
−9	F946030	NiOOH	7	23	16

greatly delimits the subsequent d-spacing search. This procedure is similar to that of Carr *et al.* (1986) in *EDSEARCH*, which was performed on the bit level to conserve storage.

The usual lower limit on Z for X-ray analysis on the transmission electron microscope (TEM) is 11 (Na), so that the elemental subsearch criteria will permit any combination of the lighter elements (Z = 1–10) to be present, including none. However, one must know all of the other elements present, or else perform multiple searches with various possible combinations of elements in mixed phases (see below). TEMs with energy-dispersive (X-ray) spectrometry (EDS) will determine elements above $Z = 10$, or above $Z = 4$ for thin window systems.

3. Input/output

3.1. Input

(*a*) Symbols for each element ($Z > 10$) present.

(*b*) The experimental error limit for $d_{\rm exp}$ (δd in %, default 1.5%). A match of a d spacing requires that

$$(100-\delta d)d_{\rm exp} \le [100d(\text{database})] \le (100+\delta d)d_{\rm exp}. \qquad (6)$$

This input parameter can be very useful in limiting the output for well calibrated d spacings.

(*c*) Two options exist: (i) a file name with path for r spacings (the radius of a ring, in cm) and then the camera length (in mm) and the electron wavelength (in nm), or (ii) the experimental d spacings $\ge$ 0.8 Å in Å (a maximum of 10).

(*d*) The required number of d-spacing matches, up to the total number of experimental d spacings entered for a single phase, or less if multiple phases are suspected.

3.2. Output

3.2.1. Summary. The output of the search, macRings, is two reports. The first, rptSummary, is opened automatically and consists of one-line summaries (CODE, FORMULA and match parameters) of matching phases sorted highest to lowest according to the figure of merit, defined as

$$\text{FOM} = \text{matching } d \text{ spacings} - \text{missing } d \text{ spacings}. \qquad (7)$$

Match parameters are defined as follows.

(*a*) 'Matching d spacings' is the number of d spacings in the database which match experimental d spacings [within error limit; equation (6)] between the highest experimental d value plus error limit and 0.8 Å minus error limit.

(*b*) 'd spacings in range' is the total number of d spacings in the database within the limits in (*a*) above.

(*c*) 'Missing d spacings' is the difference between the two numbers defined above.

Highest positive FOM numbers are best solutions. Low positive or any negative FOM numbers are highly unlikely single-phase solutions for full data sets out to d = 0.8 Å, because they have too many unobserved d values in the database. Consideration must be given to the central beam overload, experimental resolution and the lowest experimental d spacing when evaluating the output in this table.

3.2.2. Details. The second report, rptDetails, contains the complete database d-spacing listing of each potential solution with side-by-side matching experimental d spacings (where appropriate). Potential solutions are listed in the same order as in the previous report, *i.e.* in order of decreasing FOM.

A comparison of 'matching' and 'missing' d values in the database reveals the most likely solution(s). For multiple phases, matching input d spacings for the first found phase are eliminated and the search is rerun with the remaining d spacings. Elemental input is also accordingly adjusted in the second search.

4. Examples

4.1. NiO

The following nine d spacings were entered as a file of corresponding r spacings and converted to d values: 2.41, 2.08, 1.46, 1.24, 1.20, 1.04, 0.93, 0.84, 0.80 Å. Other keyboard input included the elemental symbol Ni (oxygen has too low an atomic number to be observed in X-ray analysis), an error limit of 1.5% on d, and the number of required d matches (seven here). Table 2 represents the summary (§3.2.1) output, which is contained in the database report, rptSummary. Details (§3.2.2) of each solution in the report, rptDetails, are omitted here for space (see above for description of report). The first seven solutions with highest FOMs are indis-

Table 3
RINGS tblDetails for a bismuth ceramic.

Experimental data from Carr *et al.* (1986).

CODE: 030078
Formula: $Bi_6O_{13}.xH_2O$
d spacings (Å)

Database	Experimental
9.77	
6.91	6.92
5.64	
4.89	4.98
4.37	
3.99	4.08
3.45	
3.26	
3.09	3.11
2.95	
2.82	
2.71	2.65
2.44	
2.37	2.33
2.30	2.33
2.24	
2.18	
2.13	
2.08	
1.99	1.96
1.95	1.96
1.92	1.96
1.88	
1.81	1.82

Table 4
RINGS tblDetails for a second bismuth ceramic.

Database *d* spacings < 179 Å omitted. Experimental data from Carr *et al.* (1986).

CODE: 024356
Formula: $Bi_4O_9.xH_2O$
d spacings (Å)

Database	Experimental
6.92	6.92
4.89	4.98
3.99	4.08
3.46	
3.09	3.11
2.82	
2.61	2.65
2.45	
2.37	2.33
2.31	2.33
2.19	
2.09	
2.00	1.96
1.92	1.96
1.79	1.82

tinguishable without further investigation of *d* spacings < 0.8 Å. All other solutions with FOM < 6 are unlikely, because of the large number of unobserved *d* spacings. The FOM break-point between likely and unlikely solutions is obvious. Nine of fourteen solutions are oxides of nickel; all but one of the nine have formula NiO. Slight variations in diffraction patterns and even stoichiometry (Ni_2O_3) are the result of known isomorphous structures with differing amounts of Ni^{2+} and Ni^{3+} ions (with metal ion vacancies to match the number of Ni^{3+} ions). As a group, the nickel oxide formulae match better than the others. In summary, we are quite confident of having a nickel oxide, most likely one close to the formula NiO as represented by the first seven solutions.

4.2. A bismuth ceramic

Eight diffraction rings from a bismuth ceramic (with no other elements determined) were obtained from Fig. 6 of Carr *et al.* (1986), and used as input for RINGS (3% error, 7 required matches). A total of 55 phases were found. The best solutions are shown in Tables 3 and 4, which are taken from the output report, rptDetails. As discussed below, these are not the phases found by Carr *et al.* (1986).

4.3. NiO by *EDSEARCH*

As mentioned above, *EDSEARCH* is the NIST/Sandia/ICDD search program for their Electron Diffraction Database. *EDSEARCH* output for the NiO problem described above contained 133 possible solutions, of which 11 were nickel oxides, compared with only 14 and 9, respectively, for tblSummary from RINGS (§4.1 above). *EDSEARCH* required only three *d* matches (chosen by the software, not the user) for their recommended 'Figure of Merit' minimum of 80/100 [different from equation (7) herein]. In fact, most solutions have FOM: 100, and most of these are poor matches, so the FOM is not very discriminating, as discussed below (§5). The output lists *r* spacings: the experimental ring radius (*C*/*d*, where *C* is the camera constant) rather than the more universal *d* spacing. All nine nickel oxide solutions found by RINGS in §4.1 are included in the 11 nickel oxide solutions from *EDSEARCH*, so there is some agreement between the two approaches.

4.4. A bismuth ceramic by *EDSEARCH*

EDSEARCH with the same *d*-spacing input as in §4.2 found 71 phases. Sixty-six phases were derived from NIST Crystal Data, five from the PDF. Forty-eight phases were common to the RINGS solutions (§4.2 above). Although Carr *et al.* (1986) described the solution PDF #27–53 (Crystal Data CODE 120007), Bi_2O_3, as 'perfect' in their Fig. 7 comparison, we found that only six (of eight total) experimental *d* spacings were within 3% of the PDF values. The RINGS output for this phase is found in Table 5 herein. The two unmatched *d* spacings (6.92 and 4.98 Å) were called 'hits' by Carr *et al.* because *d*/2 matched a PDF entry (see §5 below). Inspection of the full list of *d* spacings of PDF #27–53 reveals that one of these two experimental values (4.98 Å) was matched to a *d*/2 spacing, 2.498 Å in the PDF, that could not be doubled by double diffraction, *hkl* = 102 (*h* is not divisible by 2). Hence, the non-rigorous handling of double diffraction by Carr *et al.* resulted in a false hit for this *d* spacing. As mentioned in §4.2, the phases Crystal Data CODE 030078, $Bi_6O_{13}.xH_2O$, and Crystal Data CODE 024356, $Bi_4O_9.xH_2O$ (especially), are preferred, both of which match all eight experimental *d* spacings (including 6.92 and 4.98 Å) with less error. These are two very closely related cubic phases, $a = 9.77$ Å (space group

Table 5
Output of RINGS for bismuth ceramic found by Carr *et al.* (1986).

CODE: 120007
PDF: 27-0053
Formula: Bi_2O_3
d spacings (Å)

Database	Experimental
8.16	
6.91	6.92
5.38	
5.27	
4.49	
4.08	4.08
3.62	
3.51	
3.46	
3.31	
3.25	
3.18	3.11
2.92	
2.75	
2.72	2.65
2.71	2.65
2.69	2.65
2.64	2.65
2.56	
2.55	
2.53	
2.50	
2.43	
2.39	2.33
2.37	2.33

*Pn*3) and $a = 9.79$ Å (space group *Im*3), respectively; however, neither structure was fully determined. This additional information was conveniently retrieved from the respective *Access 97* tables produced from NIST Crystal Data record type E for unit cell, record type 4 for space group, and record type 1 for structure determination (Stalick & Mighell, 1986).

5. Discussion

EDSEARCH is an excellent program for the PC of the 1980s with 640 K memory and 10 Mbyte disk storage. The NIST/Sandia/ICDD Electron Diffraction Database very cleverly stores information on the bit level, which optimizes use of storage and minimizes search time. In today's PC environment, however, other considerations are more important: use of familiar desktop (including database) tools, flexible reporting, ease of transfer and reformatting of data, and ease of interpretation of output.

Comparisons with EDSEARCH follow.

(i) *Double diffraction*. In the earliest version (Carr *et al.*, 1986), the six largest experimental *d* spacings (indices *hkl*) were halved for matching against the database in the case that the original *d* spacings did not. This relaxes the match criteria too much, because *d*/2 may match a reflection other than 2*h*,2*k*,2*l*. Even though the latest version of *EDSEARCH* calculated *d* spacings for most entries (Carr *et al.*, 1989), it did not use the reduced unit cell to calculate double reflections. Some poor matches result, as seen above in the case of the bismuth ceramic.

(ii) *Experimental error limits*. With modern CCD detectors, *d* spacings can be measured to errors of 1.0–1.5% easily. This advantage is used by RINGS to delimit the possible solutions. *EDSEARCH* error limits are fixed and greater than this.

(iii) *Figure of merit (FOM)*. *EDSEARCH* only counts the number of experimental *d* spacings which match a database value to compute the FOM (Carr *et al.*, 1986):

$$\mathrm{FOM} = [200/N(N+1)]\sum_{i=1}^{N} W_i, \qquad (8)$$

where N is the number of experimental *d* spacings, i is the number of the numerically ordered *d* spacings $(1 - N)$ starting with the highest, and W_i is a weight equal to 0 if no match is found, or $N + 1 - i$ for a match.

No consideration is given to the number of database *d* spacings, within the experimental range, which have no match. This is very critical to eliminating false matches to phases with large and/or low-symmetry unit cells, for which there may be coincidental matches to experimental values, but also many unmatched database *d* spacings. As seen above, the RINGS FOM definition [equation (7)] and output ordering by FOM treats this very effectively, placing such false solutions far down on the summary report.

6. Summary and conclusions

RINGS, a comprehensive database with an efficient search program and rigorous match criteria, has been built for electron diffraction from NIST Crystal Data. Search times are typically 10–15 s on typical PCs less than four years old.

In comparison with the only previous comprehensive electron diffraction database commercially available, the NIST/Sandia/ICDD Electron Diffraction Database, RINGS has a reduced output, sorted by a rigorous figure of merit, with the implications of double diffraction fully incorporated.

A patent is pending and arrangements are underway to make the database available commercially. RINGS is intended to meet the needs of analysts in fields such as mineralogy, metallurgy, materials science, forensics, and analytical chemistry, who must identify a phase from among known well defined phases. Knowledge of crystallography is not required for its use.

Another paper in this issue (Hart, 2002) describes a second database, ZONES, for single-crystal electron diffraction, wherein two largest *d* spacings and their interangle are matched to calculated values for common zones. Again, NIST Crystal Data reduced unit cells are used to construct this database for reasons related to double diffraction as described above.

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