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# 3.3. Classification and use of powder diffraction data

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## 3.3.1. Introduction

Powder diffraction is used for many purposes. One important use is the determination of crystallographic models (crystal structures), particularly when single crystals are not available. Other common uses of powder diffraction include the identification of unknown materials; determining the amounts of different crystalline phases in a mixture; studies of phase transitions; and measuring changes in lattice constants with composition, pressure or temperature. Residual stress measurements are also frequently made using powder diffraction. Measurements of the degree of preferred orientation of grains in a processed material (texture or pole-figure measurements) are also carried out using powder diffraction; these are useful as they can be used to relate the engineering properties of a material to its processing conditions.

A wide range of instrumentation is used for powder diffraction. Synchrotron, sealed-tube and rotating-anode X-ray sources and both spallation and reactor neutron sources are used. When monochromatic radiation is used, diffraction intensities are measured as a function of the detector setting angle, $2\theta$. When polychromatic radiation is used, however, energy-dispersive detectors at fixed angles are used. For a pulsed neutron source, the neutron time-of-flight (TOF) is measured to provide energy-dispersive detection. Energy-dispersive X-ray diffraction is not common, but is used for certain specialized measurements such as *in situ* high-pressure studies. Most laboratory powder diffractometers have a single discrete detector, but a few use position-sensitive detectors (PSDs). Multiple detectors or PSDs are common for specialist instruments, for example at large national user facilities.

Historically, X-ray sensitive film in a diffraction camera was used to measure the intensities. At present, diffractometers are much more common than cameras, but film is an inexpensive method of area detection and cameras continue to have some advantages over diffractometers. X-ray film, however, has a non-linear sensitivity and a limited dynamic range, so electronic area detectors and image plates are replacing film for many applications.

## 3.3.2. Dictionary design considerations

The many applications of powder diffraction and the wide range of different instruments used dictate the design of several aspects of the powder diffraction CIF (pdCIF) data dictionary. In contrast to single-crystal measurements, where observations are reduced to instrument-independent structure factors, in powder diffraction it is not possible to interpret the data without a detailed knowledge of the type of instrument used. Another difference is that while single-crystal measurements are rarely made for any purpose other than structure determination, powder diffraction data have many non-crystallographic applications (*e.g.* identifying the phases in a mixture of unknown composition). In a single-crystal diffraction experiment, one sample yields one crystal structure. In a powder diffraction experiment, however, it is common for the sample to be a mixture of phases. Analysis of the diffraction data may result in multiple crystal structure models. It is also common to use multiple data sets, for example to fit one crystallographic model to both X-ray and neutron data simultaneously.

The powder dictionary was developed with the following basic objectives in mind. A pdCIF:

(i) should record the data-collection experiment as completely as possible and document any data analysis;

(ii) should be appropriate for the exchange of unprocessed measurements, so that it can be used in national laboratories and other shared facilities;

(iii) may contain more than one data set and/or crystal structure through the use of multiple data blocks;

(iv) may accommodate references between data blocks; and

(v) should recognize and accommodate data from as many different types of instruments as possible.

The CIF syntax, as opposed to the STAR File syntax, is not well suited to handling large multi-dimensional data sets. For some two-dimensional image formats, this deficiency was addressed by the development of imgCIF (see Chapters 2.3 and 3.7). It is also true that the CIF syntax is not well suited to storing unprocessed powder-diffraction measurements from the many instruments that use area detectors (particularly for the case of the three-dimensional data structures needed for modern TOF instruments). Even in these cases, however, diffraction intensities are commonly reduced to simpler representations, such as might be input to a Rietveld refinement program. The pdCIF definitions are intended for use with these reduced data sets.

## 3.3.3. pdCIF dictionary sections

At the time when the powder CIF dictionary was created, it was recommended practice to give data items in other dictionaries names that distinguished them from items in the core CIF dictionary. This recommendation proved cumbersome and was subsequently withdrawn, but pdCIF data items are all named in a way that distinguishes them clearly from core CIF dictionary data items: data names in the pdCIF dictionary all begin with the string `_pd_` and, likewise, the data categories in the pdCIF dictionary all begin with PD_.

The data items in the pdCIF dictionary are named according to the type of information they contain, rather than the way they will be used in a data structure. For example, data items relating to observed data have names beginning with `_pd_meas_`, even though some data items beginning with `_pd_meas_` may be assigned to the same category as items in other parts of the dictionary. The formal category assignments (see Section 3.1.10.1) were dictated by the aim to make pdCIF as versatile and simple to use as possible. As an example, one might want to put both the observed and calculated intensities in a single table (loop), as would be the case for a Rietveld refinement. This requires that the calculated and observed intensity data items are assigned to the same category. Note that this does not require that these items always appear in a single loop; calculated and observed intensity values could appear in

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Table 3.3.3.1. *Category groups defined in the powder CIF dictionary*

The groups are listed in the order in which they are described in this chapter.

| Section | Category group | Subject covered |
|---|---|---|
| (*a*) Experimental measurements | | |
| 3.3.4.1 | PD_CHAR | Characterization of a sample |
| 3.3.4.1 | PD_PREP | Preparation of a sample |
| 3.3.4.2 | PD_SPEC | Specimen used in an experiment |
| 3.3.4.3 | PD_CALIB | Calibration information |
| 3.3.4.3 | PD_INSTR | The experimental instrument |
| 3.3.4.4 | PD_MEAS | Raw measurements and instrumental settings |
| (*b*) Analysis | | |
| 3.3.5.1 | PD_PROC | Processed settings |
| 3.3.5.2 | PD_CALC | Simulated settings |
| 3.3.5.3 | PD_PEAK | Diffraction peak table |
| 3.3.5.4 | REFLN | Reflection assignments and intensities |
| (*c*) Atomicity, chemistry and structure | | |
| 3.3.6.1 | PD_PHASE | Phases present |
| (*d*) File metadata | | |
| 3.3.7.1 | PD_BLOCK | Relationships between data blocks |
| 3.3.4.3, 3.3.4.4, 3.3.5.1, 3.3.5.2 | PD_DATA | Measured and simulated intensities |

separate loops, for example, if the increment between data points differs.

This need to contain diverse items in a common 'looped' list has led the pdCIF dictionary to use category names in a different way from the other CIF dictionaries, in which CIF data items are usually named according to their category. In the pdCIF dictionary, data items that might appear in the loop for diffraction intensities are assigned to the category PD_DATA. Only one data item is named using this category as prefix, **_pd_data_point_id**. Another departure from the convention used in other dictionaries is that several **_pd_refln_*** data names are assigned to the category REFLN so that these items may be included in a loop with **_refln_*** items defined in the core CIF dictionary.

Table 3.3.3.1 summarizes the category groups in the pdCIF dictionary; the individual categories are listed alphabetically in Appendix 3.3.1. The appendix also lists for each category the section of this chapter in which the category is described.

The order in which the categories are discussed follows the scheme of Table 3.1.10.1, so that the contents of the dictionary are summarized under the headings *Experimental measurements* (Section 3.3.4), *Analysis* (Section 3.3.5), *Atomicity, chemistry and structure* (Section 3.3.6) and *File metadata* (Section 3.3.7). The pdCIF dictionary does not contribute any new data items relevant to publication beyond those already in the core CIF dictionary.

The data items in each category are listed below. Category keys, if specified, are listed first and are marked by a bullet (•); the remaining data items in each category are listed alphabetically. Note that the category PD_DATA is discussed in several different sections.

### 3.3.4. Experimental measurements

The categories in the powder CIF dictionary relating to the crystallographic experiment are as follows:

*Characterization and preparation of the sample* (§3.3.4.1)
PD_CHAR group
  PD_CHAR
PD_PREP group
  PD_PREP
*Description of the specimen* (§3.3.4.2)
PD_SPEC group
  PD_SPEC
*Instrument calibration and design* (§3.3.4.3)
PD_CALIB group
  PD_CALIB
  PD_CALIBRATION
PD_INSTR group
  PD_INSTR
*Observations and measurement conditions* (§3.3.4.4)
PD_DATA group
  PD_DATA (items beginning with **_pd_meas_***)
PD_MEAS group
  PD_MEAS_INFO
  PD_MEAS_METHOD

The pdCIF dictionary differentiates between the terms *sample* and *specimen*. The terms are often treated as interchangeable, but they have quite distinct meanings. The term sample refers to a batch of material, while the term specimen refers to the particular portion of the sample that was used for a measurement. In some cases, the specimen is modified before it is used for data collection. For example, it may be mixed with an internal standard, dried, hydrated or pressed into a pellet.

#### 3.3.4.1. Characterization and preparation of the sample

The data items in these categories are as follows:

(*a*) PD_CHAR

```
_pd_char_atten_coef_mu_calc
_pd_char_atten_coef_mu_obs
_pd_char_colour
_pd_char_particle_morphology
_pd_char_special_details
```

(*b*) PD_PREP

```
_pd_prep_conditions
_pd_prep_cool_rate
_pd_prep_pressure
_pd_prep_temperature
```

The PD_CHAR data items describe information known about the sample from observation and chemical analysis. For example, a description of the sample morphology can be specified using **_pd_char_particle_morphology**. Note that there are data items in the core dictionary that are appropriate for use with powder diffraction. For example, **_atom_type_analytical_mass_%** can be used for chemical analysis results and **_chemical_melting_point** for the melting point. Several similar data items occur in the pdCIF and core dictionaries. **_exptl_crystal_colour** and **_pd_char_colour** both describe the sample colour, but **_pd_char_colour** is more systematic. Also, **_pd_char_atten_coef_mu_calc** and **_exptl_absorpt_coefficient_mu** describe similar properties, but **_pd_char_atten_coef_mu_calc** is adjusted for the sample packing fraction, so it can be compared with the experimental value, **_pd_char_atten_coef_mu_obs**, when a direct measurement is made.

The PD_PREP data items describe how the sample was collected or prepared. For example, **_pd_prep_pressure** and **_pd_prep_temperature** describe the pressure and temperature used to prepare the sample. Note that these will probably differ from the pressure and temperature conditions at which diffraction measurements are made. Measurement conditions are recorded in **_diffrn_ambient_pressure** and **_diffrn_ambient_temperature**.