9. Identification of Crystals by X-Ray Diffraction

9.1 Principles of Identification

The structure of a crystal is essentially a three-dimensional periodic repetition of a basic structural element (the unit cell), as was shown in Section 3.2.1. The various groups of crystal planes may be identified in terms of a particular unit cell by means of indices (*hkl*) which refer to their intercepts with the axes of the unit cell. According to Eq. 4.1, the angle of diffraction 2θ for X-rays diffracted by a set of crystal planes depends upon the interplanar spacings *d*. This implies that if two different crystalline substances happen to have unit cells of the same size and shape, all the spots in the X-ray diffraction patterns of the two crystals will appear in exactly the same positions. Even if the size and shape of the unit cells are identical, however, the nature and numbers of the atoms in the cells and their spatial arrangement must be different because the substances are different. From Eq. 4.3, therefore, the diffracted intensities for corresponding crystal planes should differ. Thus, even if there is a strong superficial resemblance between the diffraction patterns of two different substances, it will always be possible to distinguish between them; there is a one-to-one correspondence between crystal and diffraction pattern. In other words, under identical conditions, crystals of the same substance will always give identical diffraction patterns (in both position and intensity), and identity of diffraction patterns is definitive evidence for identity between the diffracting crystals.

It is clear from the above that differences in the positions of the diffraction lines or spots (*i.e.* in the diffraction angles) are indicative of differences in the unit cells. Differences in the relative intensities of the various diffraction lines or spots reflect differences in the internal structures of the unit cells. It follows, therefore, as we have seen in Section 8.5, that any meaningful comparison of diffraction patterns for qualitative identifications depends upon effective standardization of all factors that affect the locations or intensities of the diffraction pattern elements.

9.2 Identification by the Powder Method

If it is possible to hazard an informed guess at the nature of the unknown substance, a simple and positive identification is often possible by comparison of its X-ray diffraction pattern with that of the substance it is thought to be.

The diffraction data of the unknown substance are generally compared with standard diffraction data. This presupposes the availability of standard X-ray diffraction data for the widest range of substances possible. The most comprehensive compilation of this type, both in quality and quantity, is the JCPDS[†1] file (former ASTM[†2] file), which is supplemented annually. There are others suitable for identifications purposes, though none on the same scale.

9.2.1 The JCPDS system

The JCPDS Powder Diffraction File (JCPDS-PDF),[1)] containing over 46,000 data on organic and inorganic compounds, is available on cards and microfiche and in book form.[1)] It should be noted, however, that from Set 37 no data on cards have been released. Electronic database on CD-ROM and magnetic tape convenient for quick search is also available.

[†1] JCPDS: Joint Committee for Powder Diffraction Standards.
[†2] ASTM: American Society for Testing and Materials.

9.2.2   Locating a JCPDS card

A. Search by computer
Rapid identification is possible by electronic computer with the aid of the JCPDS database. This database can be installed in the computer attached to most of the latest versions of the X-ray powder diffractometer, and identification can be made immediately after measurement of the diffraction patterns.

Among the search program systems, Johnson/Vand,[2] PDSM,[3] and SANDMAN[4] are well known. The Jonson/Vand program system is the earliest one, and is offered free by the JCPDS to those who purchase the JCPDS-PDF in magnetic tape: the source program is open to the public.

B. Search by hand
Indexing card(s) for a given substance can be found manually with aids such as the JCPDS Index by Hanawalt method[5] or other indexing methods such as Fink Inorganic Index and Mathews Coordinate Index (Termatrex Index).

C. Procedure for identification
The procedure to identify the unknown substances is divided into the two cases discussed below.

a) **Single phase.** If the unknown specimen consists of a single substance, and

1)   if the diffraction data observed can be located in the JCPDS-PDF, searching by hand may not be so difficult. However,

2)   if the diffraction data observed cannot be located in the JCPDS-PDF, but crystal data are obtainable elsewhere, or

3)   if the unknown specimen is a new phase, determination of unit cell parameters followed by indexing of all the diffraction patterns observed is required. Graphical method by Hull,[6] Bijurström,[7] Harrington,[8] or the methods of Hesse[9] and Lipson[10] may be used for a crystal belonging to a system with higher symmetry. For any crystal system, the use of Ito's method and related articles[11-16] is recommended. If the crystal data determined, searching will be carried out in a way similar to the identification of single crystals described below (Section 9.3).

b) **Two or more phases.** If the unknown specimen consists of two or more component substances, and

1)   if the diffraction data of all the component substances can be located in the JCPDS-PDF, hand search may take longer, and computer search is much better.

2)   If the diffraction data of one component is not found but those of the other components are found in the JCPDS-PDF, subtract the contributions of all the components identified by the JCPDS-PDF from the diffraction patterns observed, then try to identify the unknown component using residual diffraction patterns.

3)   If the diffraction data of more than two components are not found, a very rare and difficult case, try using the last method 2) described above.

In practice, the identification will be carried out in the following order:

[a) Single phase -1)] → [b) Two or more phases -1] → [a)-2)] → [a)-3)] → [b)-2)] → [b)-3)].

9.3   Identification by the Single Crystal Method

Databases of structural information on crystals, such as their lattice constants, space group, measured and calculated densities, and coordinates of the atoms in the unit cell, as well as optical and morphological data may by used for this purpose. All these databases are up-dated yearly.

9.3.1   Computer databases

A. Cambridge structural database system
Among the database systems, the Cambridge Structural Database System (CSDS), com-piled and offered by the Cambridge Crystallographic Database Center, U.K, is excellent. The CSDS system consists of two major components: the Cambridge Structural Database (CSD) and Software for Search, Retrieval, Analysis and Display of CSD contents.

The CSD is mainly a database of small organic and organometallic molecules. The CSD continues to grow in number of entries: presently the entries are more than a quarter of million, 251,515 (30 Oct. 2001) and they are expected to increase to half a million in 2010. A total of 227,181 (90.3%) entries is with $R^{\dagger} < 0.100$, which includes 202,848 (80.7%) with $R < 0.075$ [125,112] (49.7%) with $R < 0.050$ and 22,346 (8.9%) with $R < 0.030$].[17]

The software system is available in two forms: Basic software system and Graphics software system.

B. Protein data bank
The Protein Data Bank (PDB) is the single worldwide archive of primary structural data of biological macromolecules, which contains a total of 18,770 molecules (17,233 protein, peptides and viruses, 839 protein/nucleic acid compleses, 684 nucleic acids and 14 carbo-hydrates) and also a total of 3,352 NMR experimental entries (2 July 2002).[18]

C. Database for inorganic compounds and minerals and for metals and alloys
For inorganic compounds and minerals, the Inorganic Crystal Structure Database, FIZ, Germany (41,629 entries (1996)) is available[19a], and CRYSMET:CITI/NRC, Canada[19b] ($>$ 4,000 entries) can be used for the identification of metals and alloys.

9.3.2   Others

Besides the databases mentioned above, the Crystal Structure Determinative Tables[20a] may be of some help for identification purposes. These are also distributed by magnetic tape as NBS Crystal Data File,[20b] and an indexing program system, NBS*LATTICE, was released by NBS in 1986.

Strukturberichte (Vols. 1–7) succeeded by Structure Reports (Vols. 8–49 and the latest publications) and Molecular Structure and Dimensions also can be referred to for this pur-pose.

9.4   Identification of High Polymers

This is not necessarily confined to identification of the substance from the crystalline region by the usual means described above, but can extend to complete identification starting with analysis on the basis of each one of the elements of fine texture discussed in Section 7.4.

[†] for R, see Eqs. 11.38 and 11.39.

However, it is more usual simply to identify the substance from the X-ray diffractions of the crystalline region. The reader is also referred to Section 9.5.

9.4.1   Identification by unoriented X-ray patterns

There is basically no difference between this and the identification of low molecular weight substances by their powder diffraction data. In the case of high polymers, however, the diffraction lines are broadened owing to the imperfections of the crystal, and the number of lines is small. These factors, together with the superposition of the diffuse halo due to amorphous regions, make identification very difficult. Except where the diffraction pattern is very distinctive, therefore, unoriented X-ray diagrams are not often used for identification; oriented specimens are used as far as possible.

9.4.2   Identification by oriented X-ray patterns

This is the same, in principle, as identification by single-crystal X-ray diffraction. Whereas the powder method is a one-dimensional analysis making use only of the interplanar spacing d, this method involves a two-dimensional analysis of the reciprocal lattice using ξ and ζ. It should therefore be capable of higher precision than identification attempted on the basis of unoriented specimens and patterns.

Crystal data of high polymers are given by Miller.[21)]

9.5   X-Ray Diffraction Patterns of Copolymers and Polymer Blends

9.5.1   X-ray diffraction patterns of copolymers

The propensity of a copolymer to crystallize depends upon whether the monomer units A and B are three-dimensionally very similar in shape and size (as in styrene/o-fluorostyrene copolymers, cf. Table 14.2) or only moderately similar (as in ethylene/carbon monoxide copolymers, cf. Table 9.2 below), and upon any differences between the lateral dimensions of the molecular chains. There is a corresponding variety in the possible X-ray diffraction patterns displayed by copolymers, as detailed below.

   1.   The crystalline diffraction pattern of the homopolymer of just one component may be very distinct (though the lattice constants and intensities will not necessarily be those it would have displayed in isolation).

   2.   The diffraction patterns of homopolymers of A and B may be superimposed (in this case, too, the lattice constants and intensities may be modified).

   3.   A new diffraction pattern, distinct from the homopolymer of either component, may appear.

   4.   The crystallinity may disappear, whereupon the pattern will consist entirely of amorphous diffraction halos.

These are idealized categories, and the diffraction pattern is affected in practice by other factors including the following.
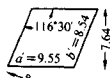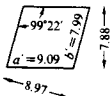
   1)   The proportions of monomer units A and B.

   2)   The mutual affinities of the monomer units of A and B (this may be thought of as their mutual solubilities).

   3)   The relative sizes of monomer units A and B.

   4)   Any difference in the crystallinities of the homopolymers of A and B.

   5)   The incidence of blocks of either A or B.

In view of the complexity of the above effects, the analysis of the X-ray diffraction patterns of copolymers can be very tedious, and a positive identification of crystals is often

much more difficult than when the identities of solid solutions of low molecular weight are being investigated. Some examples of data derived from the X-ray diffraction patterns of copolymers are given below, together with some typical patterns.

Table 9.1 shows the unit cells derived at different monomer ratios for copolymers of two monomer units whose sizes are very similar, but whose homopolymers differ in the sizes of the side chains, the numbers of repeat units per turn of the helices, and the unit cells.[22] Table 9.2[23] lists the unit cell parameters of a polyketone (ethylene/carbon monoxide copolymer).

Table 9.1   3-Methyl-1-butene/4-methyl-1-pentene copolymers[22]

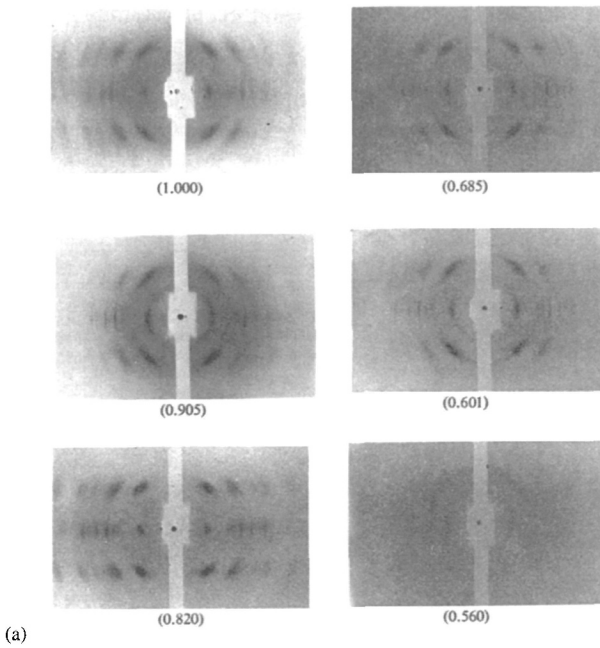| 3-Methyl-1-butene [%]	4-Methyl-1-pentene [%]	m.p. [°C]	No. of units per turn	Unit cell cross section	c [Å]
100	0	300	4/1	116°30′, a′=9.55, 8.54, 7.64	6.85
75	25	256		99°22′, a′=9.09, 8.97, 7.99, 7.88	6.85
50	50	218		90°, a′=9.27, b′=9.27	6.85
25	75	208			13.85
13	87	225			
0	100	240	3/1	90°, a′=9.27, b′=9.27	13.85

[Reproduced from F. P. Redding, E. R. Walter, *J. Polym. Sci.*, **37**, 555, John Wiley & Sons, Inc. (1959)]
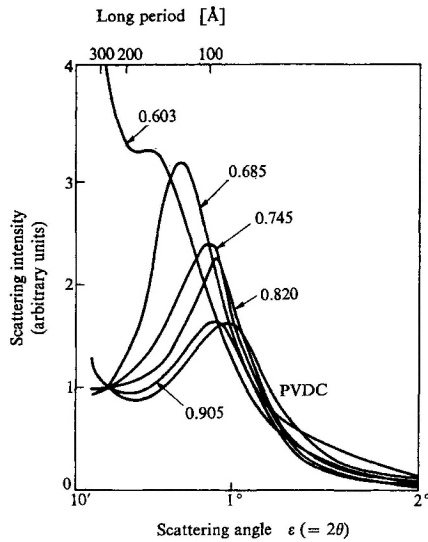
Table 9.2   Ethylene/carbon monoxide copolymers[23]

Ethylene/CO ratio	a [Å]	b [Å]	c [Å](fiber axis)
∞ (polyethylene)	7.36	4.29	2.534
3.5/1	7.53	4.91	2.54
2.2/1	7.73	4.85	2.54
1.3/1	7.86	4.81	2.54
1.1/1			7.57
1/1	7.97	4.76	7.57

[Reproduced with permission from Y. Chatani *et al.*, *J. Polym. Sci.*, **62**, S27, John Wiley & Sons, Inc. (1962)]

Figure 9.1[24] shows the diffraction patterns of some vinylidene chloride/vinyl chloride copolymers. The detailed crystal structure of copolymers presents many difficult problems, but some interesting articles on the X-ray diffraction patterns of various copolymers have been published. Examples of such articles include a paper by Beevers and White[25] on copolymers of acrylonitrile and styrene and an article by Ishibashi.[26]

(1.000)   (0.685)

(0.905)   (0.601)

(0.820)   (0.560)

(a)

(b)

Fig. 9.1   X-ray diffraction from vinylidene chloride (VDC) /vinyl chloride (VC) copolymers.[24]
(a) Wide-angle diffraction patterns—The figures refer to mole fractions of VDC. From fractions 1.000 to 0.603 the patterns change little. Crystallinity and orientation suddenly collapse at mole fraction 0.560.
(b) Small-angle scattering intensity curves—The specimens were cold drawn then heat-treated. Long period diffraction is visible down to mole fraction 0.603, but only central diffuse scattering is found at 0.560.
[Reproduced with permission from K. Okuda, *J. Polymer Sci.*, **A2**, 1749, John Wiley & Sons, Inc. (1964)]

9.5.2   X-ray diffraction patterns of polymer blends

Identification seems to be often rather simpler for blends than for copolymers. Thus the ratio of the components should be proportional to the intensities of the crystalline diffraction
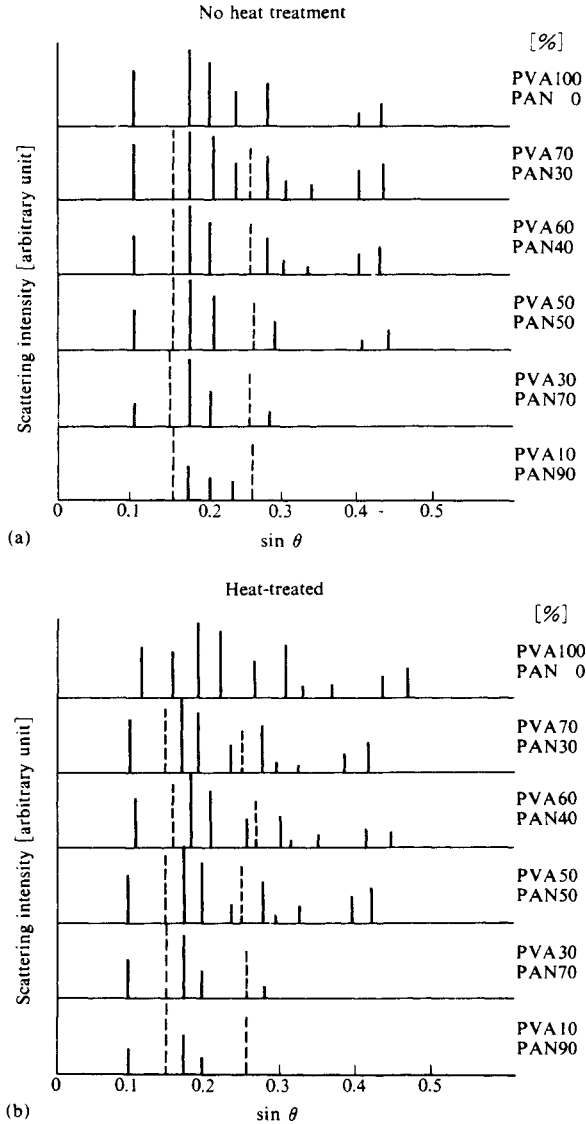

Fig. 9.2   Equatorial X-ray diffractions from PVA-PAN blended fibers.

patterns of the components. The crystal growth of the two components may, however, be affected in some cases by the degree of mutual dispersion of the component polymers, and by the interactions between polymers. If the mixing is such as to bring the molecular chains of the two components into fairly intimate contact, the eventual structure may be entirely different from any of its components. The degree to which this is observed in a particular case will obviously depend very largely upon the blending and crystallization conditions.

Since it is far easier to give an example than to talk in general terms here, we cite data for blends of poly (vinyl alcohol) (PVA) and poly (acrylonitrile) (PAN) in various ratios in Fig. 9.2. The X-ray diffraction directions are given in terms of sin θ, and the intensities represented by the length of the vertical lines, for the equatorial line. The components were dissolved in dimethylsulphoxide and spun into thread by a dry method. Diagrams are given both for specimens heat-treated for 1 h at about 100°C and for untreated specimens. It is difficult to explain the various structural changes solely with the aid of these diagrams, but the following conclusions have been established by comparison with the diffraction diagrams as a whole. Specimens that have not received heat treatment are still recognizable as blends of PVA and PAN, despite the changes in the diffraction patterns. It therefore appears that the two polymers have retained their respective structures. Some changes in the relative positions and intensities are also evident in the diffraction patterns of the heat-treated specimens except where the proportion of one component is very large. The heat treatment may have caused rearrangement of the molecules, with a change in the structure at least near the recrystallized regions. However, a detailed explanation of the structural changes on this basis alone is difficult, and we shall therefore merely note that, from the point of view of identification by X-ray diffraction, significant changes are observable.

Notes and References

1. Powder Diffraction File. Joint Committee on Powder Diffraction Standards. Diffraction data are available in card form (plain cards (3″ × 5″), keysort cards (4″ × 6″) and IBM cards) and microfiche and in book form up to Set 36, but from Set 37 no cards are available. Some of the data in the file are marked ★ to indicate a particularly high degree of accuracy, while others are marked ○ to denote less reliable data. At top left each card gives the three strongest lines and the line with the greatest interplanar spacing, together with intensities. The interplanar spacing d, relative intensities I/I_1, and indices of the various arcs are given in the right half of the card. The name, chemical formula, and structural formula of the substance are given at top right, and the experimental conditions for the diffraction data, together with crystallographic data and optical information, the method of preparing the specimen, and literature references, are given at lower left. The book form contains three cards on one page. All these diffraction data set are also available on CD-ROM and magnetic tape.
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