7.13. Powder diffraction of superconductors

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7.13.1. Introduction

In this chapter, we shall focus on the application of the powderdiffraction method to research on superconductivity, with an emphasis on using this method to obtain structural information. A great number of valuable research reports and review articles on this topic have been published in the past few decades and have been used as primary information sources in preparing this chapter. Because of space restrictions, however, only a limited number of these are given as references.

7.13.1.1. Properties of superconductors

Zero electrical resistance. Contrary to what happens in insulating, semiconducting and conducting materials, a superconductor in its superconducting state shows zero resistance to a flow of electrical current (Fig. 7.13.1*a*). T_c denotes the critical transition temperature below which the material transforms from a non-superconducting (NSC) state to the superconducting (SC) state.

Diamagnetism. Another distinguishing characteristic of superconductors is that they show diamagnetic behaviour below T_c : Figs. 7.13.1(b) and (c) show the critical field versus temperature diagrams for type-I and type-II superconductors, respectively (Lynn, 1990). For a type-I superconductor, the magnetic field is screened from the interior of the sample until a critical field H_c is reached; above H_c the superconductivity is quenched and the magnetic field penetrates uniformly into the material. For a type-II superconductor, when the applied magnetic field is less than the lower critical field H_{c1} it acts as a perfect diamagnet (like a type-I superconductor) and the field is screened from the interior bulk of the material, as shown in the SC1 region in Fig. 7.13.1(c). In the SC2 region above a critical field H_{c1} , the system is partially penetrated by the field and the material remains superconducting. The field increasingly penetrates the system as the applied field is increased, until finally above the second critical field H_{c2} the superconducting state is destroyed.

7.13.1.2. A brief description of superconducting systems

Kamerlingh Onnes (1911) first discovered superconductivity, observing that the direct current (DC) resistance of pure Hg metal droped to zero below 4.15 K. In the following years, superconductivity was found in elements, alloys, intermetallics and compounds. Bednorz & Muller (1986) reported the possible existence of a T_c of ~30 K in the La–Ba–Cu–O system. This was the first time that T_c was found to be higher than 23.2 K, previously reported for the best superconducting intermetallic Nb₃Ge thin films (Cadieu & Weaver, 1973). Since then, much effort has been devoted to superconductor research in many laboratories around the world, and hundreds of new superconductors with different structure types in different chemical systems have been successfully prepared. Cuprate hightemperature superconductors (HTSCs) are among the most interesting systems. A T_c of 93 K was found in the YBa₂Cu₃O_{7-x} system (Wu *et al.*, 1987) and a T_c of 120 K was measured for the compound Tl₂CaBa₂Cu₂O_{8+ δ} (Gao *et al.*, 1988). The highest T_c , 164 K, was observed in the HgBa₂Ca₂Cu₃O_{8+x} system under pressure at 31 GPa (Gao *et al.*, 1994). Of the many non-Cucontaining superconducting systems, the Fe-based family has attracted recent interest for its high- T_c properties. In this family, the compound NdFeAsO_{1-x}F_x has $T_c = 55$ K (Ren, Yang *et al.*, 2008). Selected superconducting systems and their years of discovery are given in Table 7.13.1. A few typical structure types are shown in Fig. 7.13.2.

The property of superconductivity relates closely to the structure type, chemical composition, the distribution of the atoms and/or ions in a material, and the temperature and pressure. Superconductivity can be shown by elements, alloys, intermetallics and chemical compounds with more complex compositions, and can be found in stoichiometric or nonstoichiometric materials.

Elements, alloys and intermetallics. Elemental superconductors can show type-I or type-II behaviour. The majority of the superconducting elements are members of the transition-metal series with a T_c as high as 9.3 K in Nb. Combinations of the transition elements with a number of other elements lead to the formation of superconducting alloys (with random atomic ordering) and intermetallic compounds [ordered crystallographically, such as Nb₃Ge (Fig. 7.13.2*a*) and MgB₂ (Fig. 7.13.2*c*)]. Fullerides (Gunnarsson, 1997; Buntar & Weber, 1996) are compounds with the general formula A_nC_{60} [the structure of an example with n = 3 is shown in Fig. 7.13.2*(b)*] and can become superconductors at high temperatures. The present record under pressure is held by Cs₃C₆₀ with $T_c = 40$ K.

Transition-metal oxides with perovskite-like and layered structures (Figs. 7.13.2e, f and g). Oxide materials are strong type-II superconductors. Most superconducting oxides contain a transition metal. T_c 's for transition-metal oxides range from low ($T_c =$ 0.7 K for SrTiO_{3-x}) to above liquid-nitrogen temperature, such as for HgBa₂Ca₂Cu₃O_{8+x}, which has a T_c of 133 K (Antipov *et al.*, 1993). Cuprate HTSCs have played a central role in the scientific and technological development of superconductors. For other



Figure 7.13.1

Definitions of superconductivity. (a) A superconductor shows zero resistance to a flow of current below T_c . The magnetic field versus temperature diagram for (b) a typical elemental type-I superconductor and (c) for a type-II superconductor. In regions SC in (b) and SC1 in (c) the material shows perfect diamagnetic behaviour and in the SC2 region the materials shows imperfect diamagnetic behaviour.

7.13. SUPERCONDUCTORS

Table 7.13.1

Selected superconducting elements, alloys, intermetallics, copper oxides, iron-based compounds and others

T = transition element, R = rare-earth element, Pn = pnictide, Ch = chalcogenide, A = alkali metal, M = alkaline-earth metal, Q = Group 15, 16 or 17 element.

Compound	T (K)	Space group $a + c(Å)$	Year of discovery	System and chemical and structural features		
Element intermetallic	and oxide su	uperconductors reported before 1986	discovery	System and chemical and structural reatures		
Hg	4.1	R3m, 3.458, 6.684	1911	Element/ I_c (K): Be/0.03, Al/1.2, Sc/0.01, 11/0.4, V/5.4,		
ru Nb	7.2 0.3	$F_{1}^{(m)}$, $F_{2}^{(m)}$, F_{2	1915	$L_{II}/0.9, Ga/1.1, L_{I}/0.0, MO/0.9, IC/7.0, Ku/0.3, Cu/0.3, In/3.4, Sn/3.7, L_2/4.0, Hf/0.1, T_2/4.3, W/0.02, P_2/1.7$		
INU	9.5	<i>Imsm</i> , 5.500	1950	III/3.4, SII/3.7, La/4.9, III/0.1, Ia/4.3, W/0.02, Ke/1.7, Ir/0.1, Tl/2.4 Lu/0.1, Th/1.4 Pa/1.4 Am/1.0		
Nb ₃ Sn	18.1	$Pm\bar{3}n. 5.291$	1954	$T_{3+r}(Sb,Al,Ge)_{1-r}$ intermetallic		
$Nb_3(Al_{0.75}Ge_{0.25})$	20-21	$Pm\bar{3}n, 5.171$	1966	J(x(-)) = J(x(-))		
Nb ₃ Ge	23.2	$Pm\bar{3}n, 5.168$	1973			
NbO	1.4	$Fm\bar{3}m$, 4.210	1964	NaCl structure: <i>T</i> (O, C, N, S)/ <i>T_c</i> (K): TiO/2.0, NbC/12, ZrS/3.3, NbN/17		
SrTiO ₂	0.7	$Pm\bar{3}m_{-}3.905$	1964	Perovskite: O-defect/mixed-valence		
$A_{x}WO_{3}$	6	Im3. 7.453	1965	Oxide: mixed-valence/A-defect		
$Li_{1+r}M_rTi_2O_4$	13	$Fd\bar{3}m, 8.405, x \simeq 0$	1973	Spinel: mixed-valence/substitution		
$Ba(Bi_{1-x}Pb_x)O_3$	13	$I4/mcm$, 6.060, 8.609, $x \simeq 0.3$	1975	Perovskite solid solution: substitution/mixed-valence		
Copper-oxide supercor	ductors with	mixed-valence state and laver-stacking struct	ure			
(La, Ba) , CuO_{i}	35	$I_{4/mmm} = 3.787 + 13.288 \text{ r} \approx 0.075$	1986	(R, M)-CuQ: mixed-valence/substitution/Cu and R		
$(La_{1-x}Da_x)_2 CuO_4$	55	1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -	1900	$(x_{1-x}, w_x)_2 \in UO_4$. Inved-valence/substitution/eu and K magnetic		
$(Nb_{1-x}Ce_x)_2CuO_{4+y}$	30	$I4/mmm$, 3.780, 13.245, $x \simeq 0.15$	1987	$(Nb_{1-x}Ce_x)_2CuO_{4+x}$: mixed-valence/substitution/		
Sr. Nd CuO.	40	$PA/mmm = 3.030 = 3.425 \ r \sim 0.14$	1001	M/R/Cu/O: mixed-valence/substitution		
$\operatorname{Bi}_{1-x}\operatorname{Ru}_x\operatorname{CuO}_2$	40 89	Amaa = 5.405 = 5.401 = 30.715	1991	Bi-Sr-Ca Cu O ₂ si mixed-valence		
YBa ₂ Cu ₂ O ₂	95	$Pmmm = 3.823 = 3.886 = 11.681 \text{ x} \sim 0$	1987	$RM_2Cu_2O_2$:: mixed-valence/O-defect and vacancy		
124204307=1	20	1.00000, 0.0	1907	ordering/Cu and R magnetic		
Tl2Ba2Ca2Cu3O10	127	I4/mmm, 3.855, 29.318	1988	$Tl_2Ba_2Ca_{n-1}Cu_nO_{2(n+1)}$: mixed-valence		
HgBa ₂ Ca ₂ Cu ₃ O _{8+x}	133	<i>P4/mmm</i> , 3.859, 12.695, $x \simeq 0.42$	1993	HgBa ₂ Ca _{n-1} Cu _n O _{2(n+1)+x} : mixed-valence/variable		
				O-content		
Fe-based and related s	uperconducto	ors containing edge-sharing TQ_4 tetrahedra				
YNi ₂ B ₂ C	17	<i>I</i> 4/ <i>mmm</i> , 3.509, 10.527	1994	$RT_{2}B_{2}C$ intermetallic: R magnetic		
YPd ₂ B ₂ C	23	<i>I</i> 4/ <i>mmm</i> , 3.710, 10.800	1994	RT_2B_2C intermetallic		
YNiBC	0.8	P4/nmm, 3.566, 7.563	1994	<i>RT</i> BC intermetallic		
La ₃ Ni ₂ B ₂ N ₃	14.6	<i>I4/mmm</i> , 3.725, 20.517	1994	R/T/B/N intermetallic		
$NdFeAsO_{1-x}F_x$	55	<i>I4/mmm</i> , 3.950, 8.537, $x \simeq 0.2$	2008	RFePnO _{1-x} F _x : mixed-valence/substitution/Fe and R magnetic		
$NdFeAsO_{1-x}$	53.5	$I4/mmm$, 3.948, 8.545, $x \simeq 0.14$	2008	RFePnO _{1-x} : mixed-valence/O-defect/Fe and R		
				magnetic		
$Ba_{1-x}K_xFe_2As_2$	38	<i>I4/mmm</i> , 3.915, 13.294, $x \simeq 0.37$	2008	$M_{1-x}A_x$ Fe ₂ Pn ₂ : mixed-valence/substitution/Fe		
K. Fe2 .Se2	32	$I_{4/m}$, 8.731, 14.113, $x \simeq 0.36$, $v \simeq 0.8$	2010	A _v Fe ₂ _v Ch ₂ _v : mixed-valence/substitution/Fe-vacancy		
rtyr c _{2=x} oc ₂	52	1000, y = 0.00, y = 0.00	2010	ordering/Fe magnetic		
LiFeAs	18	P4/nmm, 3.791, 6.364	2008	$A_{\rm x}$ FePn: mixed-valence/Fe magnetic		
$Fe_yFeTe_{1-x}Se_x$	15	<i>P4/nmm</i> , 3.801, 5.993, $x \simeq 0.57$, $y \simeq 0.03$	2008	Fe _y FeCh _{1-x} Ch' _x : mixed-valence/substitution/Fe		
LaFePO	5	P4/nmm, 3.941, 8.507	2008	RTPO		
Other superconductors		·				
MgB ₂	39	<i>P6/mmm</i> , 3.085, 3.520	2001	Borocarbides (TB, TB ₂ , T ₂ B, RB ₆ , RB ₁₂ , RTB ₂ , RT ₂ B ₂ ,		
		_		$RT_4B_4 \ etc.)$		
$RbCs_2C_{60}$	33	Fm3m, 14.555	1991	$A_n C_{60} \ (n = 3, 4, 6) / C_{60} $ buckyball		
$Na_x CoO_2 \cdot nH_2O$	4.3	P_{0_3}/mmc , 2.822, 19.768, $x = 0.31$, $n = 1.25$	2004	Hydrated: mixed-valence		
$\operatorname{MgU}_{1-x}\operatorname{Nl}_3$	8 15	$Fm5m, 5.815, X \simeq 0.98$	2001	Anuperovskite/intermetallic		
B_2 K B_1	1.3 20	$\begin{array}{c} 14/11111111, 5.0/1, 12.740 \\ Immm 12 120, 6 127, 9 662, x \sim 0.4 \end{array}$	1994	Perovskite: mixed valence/substitution		
$\operatorname{PuCoGa}_{z}$	50 18	P4/mmm 4 232 6 768	2002	RTX_{c} heavy fermion (UBe ₁₂ , $AT_{c}X_{c}$, $CeT_{c}X_{c}$)		
1 acoons	10	1 mmm, 1.252, 0.700	2002	CePt ₃ Si, UGe ₂): magnetic		

References: Poole et al. (1988); Sleight et al. (1975); Sleight (1988); Stephens et al. (1991); Cava et al. (1988); Cava, Takagi, Batlogg et al. (1994); Cava, Takagi, Zandbergen et al. (1994); Schaak et al. (2003); Blaschkowski & Meyer (2003); Bud'ko & Canfield (2006); Ren & Zhao (2009); Buzea & Yamashita (2001); Zandbergen et al. (1994); Johnston (2010).

oxides, a T_c as high as 30 K has been found in Ba_{1-x}K_xBiO₃ (Cava *et al.*, 1988). A large proportion of high- T_c superconductors are copper oxides with layer-stacking structures that contain Cu in a mixed-valence state.

Fe-based systems and borocarbides with the ThCr₂Si₂-type structure. These constitute another important family of superconducting systems. T_c has been observed to be as high as 55 K in the RFeAsO_{1-x}F_x (Fig. 7.13.2*i*) system (Ren & Zhao, 2009). These materials can be considered as interstitial derivatives of the ThCr₂Si₂-type structure in which the transition metal T is surrounded by four Q ions or atoms, forming conducting blocks of TQ_4 edge-sharing tetrahedra that alternate with chargereservoir layers (metal layers or oxide blocks). The Q ions are elements belonging to Groups 14, 15 or 16. There are two major types of materials: (i) the nonstoichiometric Fe-based pnictides or chalcogenides; and (ii) the stoichiometric intermetallics and borocarbides [such as YPd₂B₂C: see Fig. 7.13.2(*h*)] with a T_c as high as 23 K (Cava, Takagi, Batlogg *et al.*, 1994).



Typical structures for higher- T_c superconducting compounds shown in Table 7.13.1. The highest T_c reported in each system is given. (a) Nb₃Ge intermetallic; (b) RbCs₂C₆₀ 'buckyball'; (c) MgB₂ diboride; (d) the heavy-fermion superconductor PuCoGa₅; (e) intermetallic MgC_xNi₃ antiperovskite and Ba_{1-x}K_xBiO₃ perovskite; (f) (La_{1-x}Ba_x)₂CuO₄ perovskite-like layered cuprate; (g) HgBa₂Ca₂Cu₃O_{8+x} layered copper oxide; (h) YPd₂B₂C borocarbide; (i) NdFeAsO_{1-x}F_x iron-based layered compounds.

Heavy-fermion and magnetic superconductors. Heavyfermion (HF) systems are stoichiometric lanthanide or actinide compounds whose qualitative low-temperature behaviour in the normal state closely parallels that of simple metals. The HF superconductors PuCoGa₅ (Fig. 7.13.2d) (Sarrao et al., 2002) and CeCu₂Si₂ (Steglich et al., 1979) contain disordered f-electron magnetic moments on Pu and Ce. At low temperature, a strong correlation between the f-electrons and conduction electrons develops, which results in effective masses for the conduction electrons that are one or two orders of magnitude larger than the free electron mass, and strong antiferromagnetic (AFM) spin correlations exist between the *f*-electron moments themselves. These correlations may condense into an ordered AFM state of heavy electrons, or lead to heavy-electron superconductivity, or lead to the coexistence of an AFM state and superconductivity under certain conditions. In a magnetic superconductor, the system contains transition-metal or rare-earth magnetic ions. The magnetic ions influence the superconducting properties more significantly than non-magnetic impurities. Long-range magnetic order may coexist with superconductivity; this has been found in cuprates (Lynn & Skanthakumar, 2001), borocarbides (Lynn et al., 1997; Müller & Narozhnyi, 2001; Nagamatsu et al., 2001; Nagarajan, 1997) and HF and Fe-based superconductors (Lynn & Dai, 2009; Lumsden & Christianson, 2010).

7.13.2. Advantages of structure analysis from powder diffraction

Obtaining structural information is one of the central issues in research on superconductivity. In general, X-ray and neutron powder diffraction (hereafter XPD and NPD, respectively) are the most convenient and powerful techniques for obtaining such information directly, and they are widely used in laboratories around the world. There are many important reasons for preferring powder over single-crystal analysis:

- (a) In many systems it is almost impossible to grow single crystals of specified phases or compositions. Moreover, expensive equipment and a great deal of experience at crystal growing are needed.
- (b) Superconducting compounds have small unit cells and high structural symmetry and, therefore, high-quality XPD and NPD data can often be obtained conveniently under different conditions. Rietveld structure refinement (Rietveld, 1969) and related methods of data analysis allow us to determine and to refine the crystal and magnetic structures, to detect phase transformations, and to identify the phases in polycrystalline samples.
- (c) The study of powder samples is also convenient when special environmental conditions are required (low and high temperatures, high pressure *etc.*) and when diffraction,

magnetization and resistivity measurements have to be done on the sample under such special conditions.

(d) For twinned systems where the structural distortions from higher-symmetry parent structures are not large, powder diffraction can allow for more unambiguous determination of the structures of the phase, because in single-crystal diffraction there may not be sufficient resolution to isolate the diffraction from a single twin.

The Rietveld method is a whole-pattern least-squares fitting method for extracting detailed crystal and magnetic structural information from XPD and NPD data. A detailed description was given by Young (1993); see also Chapter 4.7. The method uses directly the profile intensities obtained from measurements of the powder-diffraction pattern using either a fixed angle (energy-dispersive) or a fixed wavelength (angle-dispersive). Nuclear as well as magnetic structures can be refined, and a large number of successful refinements by this method have been reported. As an example, Von Dreele & Cheetham (1974) reported a refinement of 41 structure parameters, using NPD data, for Ti₂Nb₁₀O₂₉, which has the space group *Amma* and a unit-cell volume of 2178 Å³. Experimentally, the Rietveld method is one of the most useful techniques for structural studies of superconductors.

7.13.2.1. Comparison of XPD and NPD

A good powder-diffraction pattern for structure determination and refinement using the Rietveld method should have a considerable number of independent Bragg reflections with strong intensities, precise peak positions with good resolution, and only small systematic errors.

The positions of the Bragg reflections are given by

$$2d_{\mu\nu}\sin\theta = n\lambda,\tag{7.13.1}$$

where λ is the incident-beam wavelength, *d* are the distances between successive *hkl* planes and θ are the Bragg angles of reflections, and the intensitities *I* are proportional to the square of the structure-factor amplitudes $|F_{hkl}|$:

$$I \propto |F_{hkl}|^2$$
. (7.13.2)

For X-rays

$$F_{hkl}^{2} = \left|\sum f_{j} \exp(2\pi i)(hx/a_{0} + ky/b_{0} + lz/c_{0})\right|^{2} \exp(-2W),$$
(7.13.3)

where f_j is the atomic scattering factor of atom j, a_0 , b_0 and c_0 are the unit-cell parameters and x, y, z are the fractional atomic coordinates.



Figure 7.13.3

Definition of the vectors relevant in the evaluation of the magnetic structure factor. $\boldsymbol{\varepsilon}$ and \mathbf{K} are unit vectors in the directions of the scattering and magnetic moment, respectively. The magnetic interaction vector \mathbf{q} is always perpendicular to the scattering vector.



Angular dependence of the atomic scattering amplitudes of iron for X-rays $[f_x(Fe)]$ and neutrons [b(Fe)], and of the magnetic form factors for $Fe^{2+}[f_M(Fe^{2+})]$ and $Fe^{3+}[f_M(Fe^{3+})]$. The curves were calculated using the program *GSAS* (Larson & Von Dreele, 2004).

For neutrons

$$F_{hkl}^{2} = \left|\sum b_{j} \exp(2\pi i)(hx/a_{0} + ky/b_{0} + lz/c_{0})\right|^{2} \exp(-2W),$$
(7.13.4)

where b_j is the neutron scattering length for atom j.

For magnetic scattering

$$F_{hkl}^{2} = \left|\sum \mathbf{q}_{j} f_{Mj} \exp(2\pi i)(hx/a_{0} + ky/b_{0} + lz/c_{0})\right|^{2} \exp(-2W),$$
(7.13.5)

where \mathbf{q}_j and f_{Mj} are the magnetic interaction vector and the magnetic form factor for atom *j*, respectively. $W = B(\sin^2\theta/\lambda^2)$ where *B* is the displacement parameter (Waller, 1923, 1926, 1927, 1928). The definition of **q** is indicated in Fig. 7.13.3.

In all the preceding formulas, the sums are over all the atoms in the unit cell of the structure. Fig. 7.13.4 is an example of the angular dependence of the atomic scattering amplitudes and magnetic form factors. The absolute values of the atomic scattering amplitudes for X-rays in the low-angle range of 2θ are considerably greater than those of neutrons, and this is reflected in the structure factors and in the magnitudes of the corresponding intensities of the Bragg peaks. However, the fact that the values of the atomic scattering amplitudes for neutrons remain constant as 2θ changes makes the neutron-diffraction intensities in the high-angle range comparable with those of lowangle reflections. This is an advantage when accurate measurements of displacement parameters are necessary, and to reduce correlation between displacement and occupancy parameters. The magnetic form factor for neutron diffraction is an angledependent parameter: its amplitude decreases with increasing θ . Most of the magnetic diffraction intensity, therefore, is found in the low-angle part of a diffraction pattern.

Another vitally important application of neutron diffraction is to study the magnetic structures and properties of materials. As shown in Fig. 7.13.3, the magnetic interaction vector is defined by

$$\mathbf{q} = \boldsymbol{\varepsilon}(\boldsymbol{\varepsilon} \cdot \mathbf{K}) - \mathbf{K}, \qquad (7.13.6)$$

where the scattering factor $\boldsymbol{\varepsilon}$ is a unit vector in a direction perpendicular to the effective reflecting plane and the magnetization vector **K** is a unit vector in the direction of the atomic magnetic moment. Here we have $|\mathbf{q}| = \sin \alpha$, *i.e.* the magnetic structure factor F_{hkl} will be zero when $\boldsymbol{\varepsilon}_{hkl}$ is parallel to **K**, which

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Figure 7.13.5

Schematic representation of the choice of radiation recommended for powder-diffraction experiments to obtain different structural information in research on superconductivity.

means it is possible to find the direction of an ordered magnetic moment from NPD data.

7.13.2.2. Choice of radiation

In principle, the appropriate choice of the radiation used for powder-diffraction experiments depends on whether it will provide the required information on the structure. The examples in Table 7.13.1 show that superconductors and related compounds have a great variety of chemical compositions and structure types. This can make choosing the optimal technique rather complicated. For example, in many circumstances a compound consists of heavy and light elements or atoms with similar atomic numbers at the same site in a structure. In such cases, the use of X-ray diffraction may not be appropriate, since the light atoms cannot be easily located, and the technique is not the best for distinguishing atoms with similar atomic numbers. On the other hand, XPD offers the advantage of a resolution better than that achievable with even the best neutron diffractometer, and therefore can better detect the splitting of diffraction peaks that could indicate a phase transition. NPD is not able to distinguish between elements with similar neutron-scattering amplitudes located at the same site in a structure; however, it is essential for the study of magnetic materials. Choosing the most appropriate radiation for a powder-diffraction experiment in any particular case can be facilitated by analysis of Fig. 7.13.5, a schematic representation of the usefulness of XPD and NPD.

7.13.3. Analysis of the chemical and structural features of nonstoichiometric superconductors

Determining the chemical and structural features of a superconductor will require choosing the radiation (often more than one type), designing the data-collection conditions and obtaining good powder-diffraction data in order to obtain useful and reliable information for each particular case. Many superconductors are nonstoichiometric intermetallics, solid solutions or complex compounds. A common feature of these superconductors is that the superconducting property is a function of composition. For those superconductors, structure refinement using powderdiffraction data is used to determine the chemical formula and to study the relationships between T_c and composition. The intermetallic system Nb_{3+x}Ge_{1-x} has its highest T_c of 23 K at x = 0. In the BaPb_{1-x}Bi_xO₃ solid-solution system, superconductivity was found in the composition range 0.05 < x < 0.3 (Sleight *et al.*, 1975). The compound HgBa₂Ca₂Cu₃O_{8+x} has the highest T_c of 133 K at the optimal composition x = 0.42. Moreover, for a compound having different structural modifications the powder-diffraction technique can be used to identify the structure of the superconducting phase. For example, the compound La_{1.85}Ba_{0.15}CuO₄ was found to have several modifications with different space groups, and their superconducting properties were studied (Axe et al., 1989).

7.13.3.1. Charge transfer and valence-state manipulation

Charge transfer. It has been proved that charge transfer in high- T_c cuprate and Fe-based superconductors, and in many other nonstoichiometric superconducting systems plays a very important role in their superconducting properties. A schematic view in Fig. 7.13.6 shows a sketch of the charge transfer between the conducting and the charge-reservoir layers. The electron transfer changes the charge distribution in the structure and affects the superconductivity.

In general, it is believed that the CuO₂ plane is the conducting layer responsible for the superconductivity in copper-oxide superconductors. In the Fe-based and related superconductors having the ThCr₂Si₂-type structure, the conducting layer is considered to be the $T_{1-x}Q_4$ edge-sharing tetrahedral blocks that form a two-dimensional network (T is transition metal and Q is an element from Groups 15, 16 or 17). The atom T in the conducting layer may have a mixed valence state and may form covalent, semi-covalent or ionic bonds with the O atoms. The concentration of charge carriers in the conducting layers varies when the formal charge of the transition metal T is varied. Near the conducting layer the reservoir layer acts as a charge donor to provide charge to the conducting layer. Electron transfer from the conducting layer to the charge-reservoir layer is known as 'hole doping' (on the right in Fig. 7.13.6) and moving electrons from the charge-reservoir layer to the conducting layer (on the left of Fig. 7.13.6) is known as 'electron doping'. The hole-type or electron-type charge carrier concentrations in the conducting layer are strongly related to the superconductivity. Typically, the cations in the conducting layers are transition metals that can exist in different valence states, and the cations in the



Figure 7.13.6

Schematic view of charge transfer between the conduction layer and the charge-reservoir layer in superconducting and related compounds. Electron transfer from the conducting layer to the charge-reservoir layer is known as 'hole doping' and movement of electrons from the charge-reservoir layer to the conducting layer is known as 'electron doping'.



Figure 7.13.7

Calculated atomic valence for Cu in the CuO₂ plane layer *versus* oxygen content in the chain layer of YBa₂Cu₃O_{7-x}. The bond-distance data used in the calculation are based on the structure information reported by Jorgensen *et al.* (1990).

charge-reservoir layers are rare-earth elements, alkali metals and alkaline-earth metals that have a stable valence state.

The charge transformation can be achieved by adjusting the chemical composition through substitution, doping and vacancy introduction, and can be found indirectly by analysing the valence using bond distances.

Bond-valence analysis can be used to find evidence of charge transfer. In inorganic compounds, the valence of each atom is distributed between the bonds that it forms, and it is always possible to associate a valence with each bond in such a way that the sum of the bond valences around each atom is equal to its atomic valence (Brown, 1976, 2002; Brown & Altermatt, 1985). The valence for each bond can be calculated using

$$v_{ij} = \exp[(r_0 - r_{ij})/b],$$
 (7.13.7)

where r_0 is the bond-valence parameter, which is the hypothetical length of a bond of unit valence, v_{ij} is the bond valence and r_{ij} is the experimental (Brown & Altermatt, 1985) distance between atoms *i* and *j*; the constant *b* is 0.37. The total valence V_i for an atom *i* is the sum (over *j*) of the surrounding bond valences:

$$V_i = \sum_{j=1}^{j=n} v_j,$$
 (7.13.8)

where n is the number of bonds.

Example. It is very well known that the superconducting properties are strongly related to the oxygen content in the YBa₂Cu₃O_{7-x} system. Jorgensen et al. (1990) reported the structure-property relationship for different levels of oxygen deficiency in this system with very detailed structure information obtained using NPD data. Fig. 7.13.7 shows the valence calculated using equation (7.13.8) for Cu in the conducting layer (CuO_2) as a function of the oxygen content x in the (CuO_x) layer. The behaviour is very similar to the variations of T_c as the oxygen vacancy x increases, with two plateaus being observed. In the range 0 < x < 0.35, T_c decreases from 94 to 56 K, where the calculated valence for Cu, $V_{\rm Cu}$, deceases from 2.135 to 2.108 valence units (v.u.). T_c was found to be constant with a value near 56 K for 0.35 < x < 0.45, where a corresponding plateau is observed near V_{Cu} = 2.108. Then V_{Cu} drops rapidly to about 2.082 v.u. where T_c decreases from 56 K to zero near x = 0.65.

Cation substitution in superconducting oxides. After hightemperature superconductivity was discovered in the (La,Ba)₂CuO₄ system by Bednorz & Muller (1986), Takagi *et al.* (1987) confirmed that the superconducting phase (La_{0.925}Ba_{0.075})₂CuO₄ has the K₂NiF₄-type tetragonal structure with space group *I*4/*mmm* (No. 139) at high temperature (Fig. 7.13.8*a*), with atom positions (La_{0.925}Ba_{0.075}): 4*e* (0, 0, *z*); Cu: 2*a* (0, 0, 0); O1: 4*c* (0, $\frac{1}{2}$, 0) and O2: 4*e* (0, 0, *z*). There have been many studies concerning the role of cation substitution, oxygen vacancy and structural phase transitions in the high-*T_c*



Schematic layer-stacking structures of (a) $(R_{1-x}M_x)_2$ CuO₄ and (b) HgBa₂CuO_{4+x} indicating the charge transfer between the reservoir and superconducting layers.

 $(R_{1-x-y}M_xR'_y)_2$ CuO_{4- δ} system, where *R* is a trivalent rare earth (La³⁺, Nd³⁺, Pr³⁺...) and *R'* is tetravalent Ce⁴⁺; *M* can be Ba²⁺ or Sr²⁺.

The parent compounds La₂CuO₄ and Nd₂CuO₄ are semiconductors, and have valences of 3+, 2+ and 2- for the La/Nd, Cu and O ions, respectively. Superconductivity in these materials is induced by either holes or electrons in the charge-reservoir layer. This is accomplished by partial substitution of La³⁺ or Nd^{3+} at the 4*e* site with atoms of lower or higher valences, thus making the average formal valence of the site smaller or larger than 3+. Consequently, the formal Cu valence will be larger (hole doping) or smaller (electron doping) than 2+, respectively. More specifically, in the hole-doping case, substitution of Ba²⁺ for La³⁺ will cause an electron transfer from the adjacent CuO₂ conducting layers to the chargereservoir layers, i.e. the oxidation state of copper will assume a value between 2+ and 3+. In fact, the compound La_{1.85}Ba_{0.15}CuO₄ becomes a superconductor below $T_c \simeq 30$ K by changing the formal valence of copper to 2.15+ instead of 2+. In the electron-doping case of $(Nd_{1-x}Ce_x)_2CuO_{4-\delta}$, the partial substitution of Ce⁴⁺ for Nd³⁺ and/or the presence of oxygen defects will generate an electron transfer from the reservoir to the conducting layers with consequent reduction of the copper formal valence from 2+ to between 2+ and 1+. Thus the superconducting compound Nd_{1.845}Ce_{0.155}CuO_{3.93} (Izumi et al., 1989) has the formal copper valence reduced to Cu^{1.71+}.

Remarks. Choosing the proper radiation is key for determining the superconducting composition and the doping state (electron or hole doping). In the $(La_{1-x}Ba_x)_2CuO_{4-y}$ case, it is impossible to refine the ratio of La:Ba using XPD data because Ba and La have a similar atomic numbers ($Z_{Ba} = 56$ and $Z_{La} =$ 57). However, using NPD data La and Ba can be distinguished well by Rietveld refinement because the neutron scattering amplitude of La (0.827 cm⁻¹²) is 57% larger than that of Ba (0.525 cm⁻¹²). However, the situation is more complex for the $(Nd_{1-x-y}Sr_xCe_y)_2CuO_{4+\delta}$ system, where three different elements occupy the same crystallographic site. The formal valence of copper can be larger or smaller than 2+, depending on the values of x, y and δ . Combined refinements using XPD and NPD data were able to determine the values x, y and δ as follows:

- (i) Considering that Nd ($Z_{Nd} = 58$) and Ce ($Z_{Ce} = 60$) have similar atomic numbers Z, but quite different from that of Sr ($Z_{Sr} = 38$), and the amount of Ce in the compound is much less than the amount of Nd, the formula can be simplified to [(Nd/Ce)_{1-x}Sr_x]₂CuO_{4- δ} and x can be obtained from refinement using XPD data.
- (ii) Fixing the x value obtained from step (i), the y value can be obtained from refinement using NPD data, where the difference in the neutron scattering amplitude between Ce (0.484 cm^{-12}) and Nd (0.769 cm^{-12}) is large.
- (iii) The NPD data can be used to refine the oxygen vacancy δ , because O has a comparable neutron scattering amplitude (0.525 cm⁻¹²) to that of the cations.

Oxygen stoichiometry in superconducting cuprates and oxides. It is accepted that the oxygen stoichiometry dramatically affects the properties of HTSCs in most non-stoichiometric superconducting cuprates and oxides. In the HgBa₂Ca_{*n*-1}Cu_{*n*}O_{2(*n*+1)+x} system, the parent compounds (x = 0)



(a) Schematic view of electron transfer in Fe-based superconducting and related compounds. It is believed that the block of edge-sharing TQ_4 tetrahedra contributes to the superconductivity. (b) $AE_{1-x}A_xFe_2Pn_2$ (Rotter *et al.*, 2008) and $A_yFe_{2-x}Ch_2$, where AE are alkaline-earth metals and A are alkali metals; (c) RFeAsO_{1-x}F_x; and (d) phases, Sr₂MFePnO₃, where M = Sc, Ti, V.

are all non-superconductors. When x = 0.06, the n = 1 compound HgBa₂CuO_{4+x} has a T_c of 94 K (Fig. 7.13.8*b*) (Putilin *et al.*, 1993). The non-superconducting parent compound HgBa₂CuO₄ (x = 0) has Hg²⁺, Ba²⁺, Cu²⁺ and O²⁻. By adding oxygen atoms to the HgO_x charge-reservoir layer, the formal copper valence is increased from Cu²⁺ to Cu^{(2+ δ)+} and the compound becomes a hole-doped superconductor. In this system T_c has been found to be as high as 133 K (Antipov *et al.*, 1993; Chmaissem *et al.*, 1993) for the n = 3 compound HgBa₂Ca₂Cu₃O_{8+x} with x = 0.42, *i.e.* the additional 0.42 oxygen atoms increase the formal copper valence from Cu²⁺ to Cu^{2.26+}.

Remarks: Compared with the metal atoms in these nonstoichiometric superconducting cuprates and oxides, oxygen is a light element and has a smaller X-ray scattering amplitude. Therefore, NPD data were needed to refine the oxygen occupancy, since the neutron scattering amplitude of O is similar to those of the metal atoms.

Cation and anion substitution in Fe-based superconductors. The Fe-based pnictide (Pn) and chalcogenide (Ch) families have Fe-containing layers in which the Fe atoms are coordinated by four pnictogen or chalcogen (Q) ions forming a block of FeQ₄ edge-sharing tetrahedra. The first superconductor observed in this system was LaFePO ($T_c = 5$ K), found by Kamihara *et al.* (2006). On replacing P by As, T_c increases to 26 K in the LaFeAs(O_{1-x}F_x) system (Kamihara *et al.*, 2008). Soon after, a series of related superconductors were reported in the RFeAs(O_{1-x}F_x) and RFeAsO_x systems with a maximum T_c of up to 55 K (Ren, Yang *et al.*, 2008; Ren, Che *et al.*, 2008).

Fe–Pn(Ch) compounds have high chemical and structural flexibility for a large variety of constituent elements. Like the high- T_c cuprates, where Cu has a mixed valence in the conducting

Table 7.13.2

Selected layered copper-oxide superconductors

n is the number of CuO₂ conducting layers per formula unit.

Formula	п	T_{c} (K)	Charge-reservoir unit	CuO ₂ conducting layer and blocks
$Sr_{1-x}Nd_xCuO_2$	1	40	$[\mathrm{Sr}_{1-x}\mathrm{Nd}_x]$	CuO ₂
$(R_{1-x}M_x)_2$ CuO ₄	1	35	$[R_{1-x}M_x - O_2 - R_{1-x}M_x]$	CuO ₂
$La_{2-x}M_xCa_{n-1}Cu_nO_{2n+1}$	1, 2	35, 60	[(La,M)O-(La,Ca)O]	CuO ₂ -Ca-CuO ₂
$Nd_{2-x-y}Ce_xSr_yCuO_4$	1	28	$[Nd_{2-x-y}Ce_xSr_y-O_2-Nd_{2-x-y}Ce_xSr_y]$	CuO ₂
$YBa_2Cu_3O_{7-x}$	3	90	BaO [CuO_x] BaO	CuO ₂ -Y-CuO ₂
YBa ₂ Cu ₄ O ₈	4	80	BaO $[CuO_x]$ BaO	CuO ₂ -BaO-CuO ₂ -Y-CuO ₂ -Y-CuO ₂ -BaO-CuO ₂
$HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$	1, 2, 3, 4, 5	94, 112, 133,	$BaO [HgO_x] BaO$	CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂
		130, 100		
$Tl_{1-y}Ba_2Ca_{n-1}Cu_nO_{2n+3-x}$	1, 2, 3, 4, 5	50, 90, 110,	BaO $[TlO_x]$ BaO	CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂
-		122, 117		
$Tl_{2-y}Ba_2Ca_{n-1}Cu_nO_{2n+4-x}$	1, 2, 3, 4	80, 110, 125,	BaO $[TlO_x-TlO_x]$ BaO	CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂
-		113		
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$	1, 2, 3	22, 85, 110	$SrO [BiO_x - BiO_x] SrO$	CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂
$(Pb_2Cu)Sr_2(Ca,Y)_{n-1}Cu_nO_{2n+4}$	1, 2	32, 70	$SrO [PbO_x-CuO_x-PbO_x] SrO$	CuO_2 -(Y, Ca)-CuO ₂
$(Cu/C)_2Ba_2Ca_{n-1}Cu_nO_{2n+2}$	3, 4, 5	72, 117, 95	BaO [(Cu/C)O-(Cu/C)O] BaO	CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂
$Cu_yBa_2Ca_{n-1}Cu_nO_{2n+3-x}$	3, 4	120, 117	$BaO [Cu_x] BaO$	CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂ -Ca-CuO ₂

References: Cava (2000); Park & Snyder (1995); Hauck & Mika (1998); Tokura & Arima (1990); Parkin et al. (1988).

layers, the formal valence for iron can be adjusted from Fe^{2+} to $Fe^{(2\pm\delta)+}$ when electrons are transferred between the conducting and charge-reservoir layers, as shown in Fig. 7.13.9(a). Changing the valence state of Fe can be achieved by cation or anion doping. The layer or block between the blocks of FeAs(Se)₄ edge-sharing tetrahedra is the charge-reservoir unit: it can be a simple layer (Fig. 7.13.9b) or complex blocks (Figs. 7.13.9c, 7.13.9d). For the $Ba_{1-x}K_xFe_2As_2$ system shown in Fig. 7.13.9(b), the parent compound BaFe₂As₂ (x = 0) contains Ba²⁺, Fe²⁺ and As³⁻ and is not a superconductor. Partial substitution of Ba²⁺ with the lowervalence cation K¹⁺ will make the average formal valence for Fe larger than 2+ and the compound becomes a superconductor. In the RFeAs($O_{1-x}F_x$) system (Fig. 7.13.9*c*), the superconductivity can be introduced by electron doping when the formal valence for Fe is adjusted to be smaller than 2+ through partial replacement of F^{1-} with O^{2-} .

Remarks. As Ba has a higher atomic number than K but the neutron scattering amplitudes for Ba and K are very similar, XPD data should be better than NPD data for determining the K content in $(Ba_{1-x}K_x)Fe_2As_2$ compounds. On the other hand, neither XPD nor NPD data can be used to obtain the F content when replacing O by F in the *R*FeAs $(O_{1-x}F_x)$ system because of the small difference in both the numbers of electrons and the neutron scattering amplitudes for O and F.

7.13.3.2. Modelling of layer structures

Stacked layers are widely found in the structures of the cuprate superconductors and are used to explain the charge transfer. The structural features of the layered superconducting copper oxides and of related materials have been described in many reviews (Sleight, 1988; Tokura & Arima, 1990; Park & Snyder, 1995; Raveau *et al.*, 2013). Selected high- T_c copper-oxide systems with the stacking described below are shown in Table 7.13.2. These structures are formed by stacking layers of the conducting and intermediate layers. The intermediate layers can be charge-reservoir or 'regulation' layers. In the structures of $(R_{1-x}M_x)_2$ CuO₄ and HgBa₂CuO_{4+x}, illustrated in Fig. 7.13.8, the CuO₂ plane is the conducting layer, and $(R_{1-x}M_x)O_y$ and HgO_x are the charge-reservoir layers. The BaO layer in HgBa₂CuO_{4+x} is a regulation layer where the occupancies and valences of Ba and O remain unchanged. The structure is constructed by the following layer-stacking sequences:

 $(R_{1-x}M_x)_2$ CuO₄: {CuO₂}_O $[R_{1-x}M_xO]_C$ $[R_{1-x}M_xO]_O$ {CuO₂}_C $[R_{1-x}M_xO]_O$ $[R_{1-x}M_xO]_C$ {CuO₂}_O...

HgBa₂CuO_{4+x}: {CuO₂}_O (BaO)_C [HgO_x]_O (BaO)_C {CuO₂}_O.

The chemical symbols enclosed in braces, square brackets and parentheses express the actual compositions of the conducting, charge-reservoir and regulation layers, respectively, and the subscripts *O* and *C* indicate whether the cation is located at the origin or at the centre, respectively, of the net of the layer. In $(R_{1-x}M_x)_2$ CuO₄, the conducting CuO₂ layers sandwich the $R_{1-x}M_x$ O charge-reservoir layers in alternating stacking along the *c* axis. A few typical layer structures are illustrated in Fig. 7.13.10. Fig. 7.13.11 shows the stacking structure along the *c* axis of the HgBa₂Ca_{n-1}Cu_nO_{2(n+1)+x} (*n* = 1, 2, 3, 4, 5, 6) series of superconductors. The structures can be constructed in the following way, where the charge-reservoir unit is shown in bold: ... {CuO₂}_O (Ca)_C {CuO₂}_O (**BaO**)_C [**HgO**_x]_O (**BaO**)_C {CuO₂}_O (Ca)_C {CuO₂}_O...

Using the charge-reservoir unit as a centre, the CuO_2 and the Ca layers are stacked alternately along the *c* axis. The Ca layers



(b) Charge reservoir or regulation layers

Figure 7.13.10

Layers in copper-oxide high- T_c superconductors. (a) Typical conduction layers CuO and CuO₂ in cuprate families which are considered to be responsible for the superconductivity. (b) Selected layers that act as charge-reservoir or structure-regulation layers present in copper-oxide superconductors. The subscripts O and C indicate whether the cation is located at the origin or at the centre of the net of the layer, respectively. Selected examples for the reservoir layers are shown in Table 7.13.2.



Figure 7.13.11

Structure stacking along the *c* axis for the HgBa₂Ca_{n-1}Cu_nO_{2(n+2)+x} series of superconductors.

do not act as donors of charge carriers and only play the role of regulation layers for the geometric requirements of the structure. T_c depends on the oxygen content in the HgO_x charge-reservoir layer, and is strongly correlated with the number of CuO₂ layers.

7.13.3.3. Structural transformations

Above T_c , a superconductor may be an electron insulator, a semiconductor or a metallic conductor. Changes in the electrontransport behaviour are in some cases accompanied by structural modifications due to structure distortions, chemical orderdisorder and/or variations in composition. The different structures may belong to different crystal systems, or belong to the same crystal system but have different space groups; this can be determined by analysing the powder-diffraction pattern. Fig. 7.13.12 shows some examples of possible diffraction-peak positions calculated by considering only the primitive lattice. [Symmetry relations between space groups during structural distortions are discussed in *International Tables for Crystallography*, Volume A1 (2011).] For data collection, the high resolution available for XPD (especially at a synchrotron) is beneficial for detecting the peak splittings that result from a small lattice distortion, and NPD has an advantage in measuring superstructure peaks where intensities come from small shifts of light elements.

Perovskite-like structure distortions. Superconductivity has been found in many compounds with perovskite-like structures. An ideal perovskite has the chemical formula ABX_3 with cubic $Pm\bar{3}m$ symmetry and with atomic positions $A: 1a \ (0, 0, 0), B: 1b \ (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $X: 3c \ (\frac{1}{2}, \frac{1}{2}, 0)$ [see Fig. 7.13.2(*e*)]. In practice it has been found that the perovskite structure exists if $0.75 \le p \le 1.0$, where

$$p = (r_A + r_X)/[2^{1/2}(r_B + r_X)];$$

p is Goldschmidt's tolerance factor (Goldschmidt, 1926) and r_A , r_B and r_X are the ionic radii (Shannon, 1976) of A, B and X, respectively. The A and B ions are located at the corners and at the centre of the cubic unit cell. respectively. The ions X are located at the centre of the six faces of the cubic cell and form an octahedron around the *B* cation. Each octahedron shares corners with the nearest neighbours. The distortion of the octahedra and/ or their tilting results in different modifications of the ideal structure. Fig. 7.13.13 shows an example in which the octahedron at the centre and the four surrounding octahedra are rotated in opposite directions around the cubic c axis. Such rotations are responsible for a lowering of the symmetry from cubic to trigonal, tetragonal, orthorhombic or monoclinic (Glazer, 1972, 1975). The distortions can be temperature and/or composition dependent, as happens in the perovskitelike system (La,Ba)₂CuO₄ (Axe et al., 1989) as well as in BaBi_{1-r}Pb_rO₃ (Cox & Sleight, 1976; Marx et al., 1992).

Tetrahedral distortions. A structural transition due to polyhedral distortion is also present in Fe-based superconductors. As an example, the parent compound LaFeAsO of the LaFeAsO_{1-x} F_x superconductor has a structure with *P*4/*nmm* symmetry and lattice parameters

 $a_t = 4.03007$ (9) Å and $c_t = 8.7368$ (2) Å at 175 K (Nomura *et al.*, 2008). The polyhedral distortion breaks the tetragonal symmetry below 155 K and the material becomes orthorhombic with *Cmma* symmetry. The axes transformation from the tetragonal to the orthorhombic phase is $(a_o \ b_o \ c_o) = (110/\overline{110}/001)(a_t \ b_t \ c_t)$, and the relation between the lattice parameters of the two phases is $a_o \simeq b_o \simeq 2^{1/2}a_t$ and $c_o \simeq c_t$. In this case, peak splitting and superlattice peaks will be present in the powder pattern.

Stoichiometry dependence and vacancy ordering. Orderdisorder transitions can be induced by external forces (temperature and pressure) and/or internal forces (chemical composition). Chemical order-disorder is present in both the cuprate and Fe-based high- T_c superconducting families, as observed in the YBa₂Cu₃O_{7-x} and K_xFe_{2-y}Se₂ systems.

The crystal structure and phase transition of YBa₂Cu₃O_{7-x} have been studied carefully with the Rietveld method, using both XPD and NPD data (Cava *et al.*, 1987; Jorgensen *et al.*, 1987, 1990). The results revealed the presence of oxygen vacancies in the CuO_{1-x} charge layer (see Fig. 7.13.14*a*) and the structure undergoes an orthorhombic *Pmmm* to a tetragonal *P4/mmm*



Figure 7.13.12

Schematic plot of the possible diffraction peaks with consideration of the primitive lattice only. The thick red lines are the reflections corresponding to a cubic lattice, and the thin blue lines are the reflections due to the peak splitting or the superlattice peaks. (a) Reflections from a simple cubic lattice; (b), (c) and (d) reflections from tetragonal, orthorhombic and monoclinic lattices, respectively. As a result of the lattice distortion, a cubic peak may be split into two or more peaks; in (e) and (f) reflections show the presence of peak splitting and also superlattice peaks (such as the peaks for *hkl* with l = odd) from the superlattice.

transition. The transition is induced by a change in the oxygen stoichiometry and is a function of temperature. The orthorhombic phase exists over the range $0 \le x < 0.65$, with the oxygen vacancies along the *a* axis. The remaining oxygen atoms form chains along the *b* axis within square-planar CuO₄ motifs, coordinated in the *b*-*c* plane (Fig. 7.13.14*b*). The vacancies are disordered in the tetragonal phase ($x > \sim 0.65$), thus destroying



Figure 7.13.13

A structural transformation induced by a rotation of the octahedra in the perovskite structure. A projection along the *c* direction, showing that the rotation of the corner-shared octahedra is responsible for the symmetry change and for the formation of a superstructure in which $a_s = b_s = 2^{1/2}a_p$ and $c_s = c_p$, where a_p (= $b_p = c_p$) is the lattice parameter for the cubic perovskite and a_s , b_s and c_s are the parameters of the superlattice.

the Cu–O chains of the orthorhombic modification (Fig. 7.13.14c).

Structural transitions are observed due to the iron-vacancy ordering in the $A_x \text{Fe}_{2-v} \text{Se}_2$ system. Guo *et al.* (2010) first reported a T_c of 31 K in K_xFe_{2-v}Se₂. Different iron-vacancy ordering models have been reported in compounds with A = K, Rb, Tl/Rb and Tl/K (Fig. 7.13.15). Structure analysis of the compound K_{0.83(2)}Fe_{1.64(1)}Se₂ (Bao et al., 2011) using NPD data indicated that at 580 K the compound has the tetragonal ThCr₂Si₂type structure (I4/mmm) with lattice parameters $a_{t1} = b_{t1} =$ 3.94502 (7) Å and $c_{t1} = 14.1619$ (4) Å. A long-range Fe-vacancy ordering occurs below 578 K (Fig. 7.13.15b), with a consequent structural transition from the I4/mmm phase (t1) to a tetragonal I4/m superstructure phase (t2) with parameters $a_{t2} = b_{t2} \simeq 5^{1/2} a_{t1}$ = 8.6929 (2) Å and $c_{t2} \simeq c_{t1} = 14.0168$ (4) Å at 11 K. In this structure model the ideal composition should be KFe₄Se₅ where for every five possible Fe positions there is one vacancy. Another model for the long-range Fe-vacancy order [Fig. 7.13.15(c1)] was proposed by Fang et al. (2011) and Kazakov et al. (2011) for compounds with an ideal composition AFe₃Se₄. In this model, for every four possible Fe positions there is one vacancy and consequently the superlattice has orthorhombic symmetry with unit-cell parameters $a_o \simeq 2^{1/2} a_{t1}$, $b_o \simeq 2(2^{1/2}) a_{t1}$ and $c_o \simeq c_{t1}$. The models in Figs. 7.13.15(c1) and 7.13.15(c2) are the two local configurations; they have the same symmetry and cannot be distinguished by Rietveld refinement. If the two configurations



Figure 7.13.14

Structural transformation from tetragonal P4/mmm symmetry to orthorhombic Pmmm symmetry due to oxygen vacancy ordering in the CuO_{1-x} charge-reservoir layer. (a) Crystal structure of YBa₂Cu₃O_{7-x}. (b) The structure has orthorhombic symmetry when long-range oxygen-vacancy ordering occurs in the charge-reservoir layer, leaving the Cu in a CuO_4 square-planar configuration in which the Cu-O atoms form chains along the *b* axis of the unit cell. (c) In the range $0.65 < x \le 1$ the structure has tetragonal symmetry, in which the oxygen vacancies are disordered, thus fragmenting the one-dimensional Cu-O chains.

are present in equal amounts, one will get an average structure from powder diffraction. Therefore, the structure has an orthorhombic superlattice which is related to the tetragonal modification by the relations $a_o' \simeq b_o' \simeq 2^{1/2}a_{t1}$ and $c_o' \simeq c_{t1}$, as shown in Fig. 7.13.15(c).

Remarks. Since powder diffraction measures the average long-range-ordered structure, the local short-range-ordered structure might not be detected. In the A_x Fe_{2-v}Se₂ system, the



Figure 7.13.15

Possible vacancy-ordering arrangements in the Fe plane for $A_x \text{Fe}_{2-y} \text{Se}_2$. (*a*) At high temperature the compound has no vacancies and forms the ThCr₂Si₂-type structure (*I4/mmm*). (*b*) One type of vacancy-ordering arrangement in the composition near $A_x \text{Fe}_4 \text{Se}_5$ where for every five Fe positions there is one vacancy. (*c*1), (*c*2) A proposed type of local vacancy-ordering configuration for the composition near $A_x \text{Fe}_3 \text{Se}_4$ where only three-quarters of the possible Fe positions are occupied (Fang *et al.*, 2011; Kazakov *et al.*, 2011). (*c*) In a powder-diffraction experiment, the pattern will show the average of the (*c*1) and (*c*2) domains resulting in an orthorhombic *Pmna* symmetry. compositions of the compounds are very variable and the long-range Fe-vacancy ordering is achieved by diffusion in the solid state at a relatively low temperature. One cannot expect to reach a complete long-range Fe-vacancy order and a homogeneous distribution of vacancies in a bulk sample or a single crystal. The local structure, therefore, could be very complicated. The electron-diffraction method and/or pair distribution function (PDF) analysis can be used to obtain local structure information.

Substitution effects. In the LaFeAs($O_{1-x}F_x$) system, the parent compound (x = 0) has tetragonal P4/nmm symmetry at room temperature and an orthorhombic Cmma lattice at low temperature. However, the tetragonal P4/nmm phase is stabilized at low temperatures by partial replacement by fluorine for oxygen, *i.e.* by adjusting the dopant F concentration x (Zhao et al., 2008; Huang et al., 2008).

7.13.4. Magnetic order in superconductors and parent compounds

The interaction between superconductivity and magnetic properties is one of the most striking physical phenomena in this field. In a superconductor, in general, electrons can be in a superconducting state and/or in a magnetic state at low temperature. The study of the effects associated with the interaction between superconductivity and magnetism is a very active area of research for understanding the mechanism of superconductivity and whether superconductivity and magnetic order can coexist microscopically. Scientists have invested significant effort in investigating the magnetic properties of superconductors using different techniques, focusing on the high- T_c superconducting systems such the layered cuprates (Lynn & Skanthakumar, 2001; Niewa *et al.*, 2011), Fe-based compounds, borocarbides (Müller & Narozhnyi, 2001; de la Cruz *et al.*, 2008) and HF superconductors. Common features of the magnetic structures are:



Figure 7.13.16

Representation of selected commensurate ferromagnetic and antiferromagnetic ordering schemes. Arrows show the magnitudes and directions of the moments. The crystallographic primitive unit cell is indicated by solid lines and the dotted lines show a possible magnetic unit cell. $a_N = b_N$ are the lattice parameters for the nuclear structure and a_M and b_M are those of the magnetic unit cell. (a) Ferromagnetic order; (b) a ferrimagnetic order; (c) a canted ferromagnetic order; (d) a collinear antiferromagnetic order; (e) a canted non-collinear antiferromagnetic order where both the \mathbf{M}_x and \mathbf{M}_y directions have antiparallel components; (f) an example of a triangular antiferromagnetic structure in hexagonal and trigonal crystals.

- (i) Long-range antiferromagnetic ordering is present in some superconductors and related compounds containing rareearth elements and/or transition metals.
- (ii) In transition-metal compounds the ordering occurs at much higher temperatures and with considerably smaller moments than for compounds containing rare-earth elements. The ordering also occurs at much higher temperatures in compounds containing both types of elements.
- (iii) Magnetic ordering is strongly correlated to chemical composition (including replacement and doping), crystal structure and superconductivity.
- (iv) Magnetic ordering in some compounds containing rare-earth elements can coexist with superconductivity. It is questionable whether such coexistence can be present for transition metals located in the conducting layers.

NPD is essential for investigating magnetic materials, *e.g.* to determine the long-range order of magnetic structures and to measure the ordered magnetic moments (Cox, 1972).

7.13.5. Conclusions

Superconductivity can be shown by elements, alloys, intermetallics and chemical compounds of more complex compositions, and can be found in either stoichiometric or nonstoichiometric compounds. In general, the properties of superconductivity depend on the structure, *i.e.* the symmetry, the chemical composition, and the distribution of the atoms and/or ions in the structure under particular conditions (such as temperature, magnetic field and pressure). Powder diffraction has been widely and effectively employed to provide structural information and, combined with other tools or special techniques, to reveal the relationships between structure and superconductivity. As in many other research fields in materials science, powder diffraction is used to identify and to characterize the phase, to find the optimal composition, to study phase diagrams, and to determine the crystal and magnetic structures.

APPENDIX A7.13.1 The study of long-range magnetic order in superconductors

Magnetic properties have been described briefly by Borovik-Romanov et al. in Chapter 1.5 of International Tables for Crystallography Volume D (2013). Like crystal structures, the parameters of magnetic structures include the magnetic unit cell, the lattice, the magnetic moments, the symmetry elements and the space group. The moments can be arranged in parallel and antiparallel configurations, and the 14 Bravais lattices of classical crystallography become 36 magnetic lattices (Zamorzaev, 1957*a*,*b*). An additional element, 'antisymmetry', is produced by introducing the time (or current) reversal operator R, which acts in combination with a normal symmetry operation. With the antisymmetry element, and based on the symmetry of the 230 space groups, 1651 magnetic space groups (Shubnikov groups) have been derived [Shubnikov (1951); Belov et al. (1957); see also Chapter 3.6 in International Tables for Crystallography Volume A (Litvin, 2016)]. This section deals only with the basic magnetic crystallography related to investigations of long-range magnetic order in superconductors and in related materials, analysed using NPD.

A7.13.1.1. Commensurate magnetic ordering and primitive cells

The periodicity of a magnetic unit cell is consistent with the arrangement of the magnetic moments in addition to that of the atomic distribution. A schematic representation of the simplest types of ferromagnetic and antiferromagnetic moment arrangements (Fig. 7.13.16) helps to show the relationship between the

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Table 7.13.3

Crystal systems, conventional coordinate systems and the 36 magnetic lattices in three dimensions

In the orthorhombic system, lattices with a different white lattice and location of black lattice (as indicated by the subscript) are shown in parentheses (see Section A7.13.1.2).

		Conventional coordinate system		Symbols of the 36 magnetic lattices	
System	Symbol	Restrictions on cell parameters	Parameters to be determined	White	White and black
Triclinic	а		$a, b, c, \alpha, \beta, \gamma$	aP	aP_s
Monoclinic	т	$\alpha = \gamma = 90^{\circ}$	a, b, c, β	mP, mC	$mP_b, mP_a, mP_C, mC_c, mC_a$
Orthorhombic	0	$\alpha = \beta = \gamma = 90^{\circ}$	a, b, c	oP, oI, oF (oC, oA)	$oP_I, oF_s, oI_c (oP_C, oP_A)$
					$ \begin{array}{c} (oC_A, oA_C) (oP_c, oP_a) \\ (oC_c, oA_a) (oC_a, oA_c) \end{array} $
Tetragonal	t	$a = b, \alpha = \beta = \gamma = 90^{\circ}$	$a = b \neq c$	tP, tI	tP_c, tP_C, tP_I, tI_c
Trigonal	h	$a = b = c, \alpha = \beta = \gamma$	α, α	hR	hR_I
Hexagonal	h	$a = b, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	a, c	hP	hP_c
Cubic	С	$a = b = c, \alpha = \beta = \gamma = 90^{\circ}$		cP, cF, cI	cP_I, cF_s

unit cells of the nuclear and magnetic structures. For simplicity, only the *ab* plane in a tetragonal [(a)-(e)] and a hexagonal (f) structure is shown $(a_N = b_N$ are the nuclear and a_M and b_M are the magnetic unit-cell parameters).

Ferromagnetic ordering (Fig. 7.13.16*a*). Ferromagnetic order often involves only one kind of magnetic ion or atom and the spontaneous magnetization is uniform $(\mu_1 = \mu_2)$, *i.e.* their magnetic moments have the same amplitude and are aligned parallel and in the same direction to each other. In this case, the magnetic structure has the same unit cell as the nuclear unit cell, *i.e.* $a_N = a_M$ and $b_N = b_M$. Therefore, it should be possible to index the magnetic reflections in an NPD pattern using the nuclear unit cell and the magnetic intensities will overlap with the nuclear peaks.

Ferrimagnetic ordering (Fig. 7.13.16*b*). In this example of ferrimagnetic order, all the moments have parallel alignment but

have different amplitudes. The magnetic ions or atoms at the corners of the nuclear unit cell are aligned antiferromagnetically and have different moment amplitudes to the ones at the centre. The system has a net ferromagnetic moment $\mu = \mu_1 - \mu_2 + \mu_3 = \mu_3$. The magnetic unit cell can be $a_M = 2a_N$ and $b_M = 2b_N$ or $a_M = b_M = 2^{1/2}a_N$ (indicated by dotted lines). In this case magnetic reflections corresponding to the magnetic superlattice should be observed in the NPD pattern.

Canted ferromagnetic ordering (Fig. 7.13.16c). The canted ferromagnetic order shown in the figure is a simple non-collinear structure generated by the tilting of the μ_1 and μ_2 moments. In this case the system possesses a net ferromagnetic moment; components in the \mathbf{M}_x direction are ferromagnetic and the moment component in the \mathbf{M}_y direction has an antiferromagnetic arrangement. The magnetic unit cell can be obtained by doubling a_N and b_N , or $a_M = b_M = 2^{1/2} a_N$ (dotted lines). The canted



Figure 7.13.17

Types of magnetic lattices. The first row are the five white lattices P, C, A, I and F. The other white-and-black lattices can be constructed by combination of a white lattice with its corresponding black lattice, with the black lattice having its origin at the face centre or edge centre or body centre of the white lattice [indicated by the subscript, see (e)].



Figure 7.13.18

Selected magnetic symmetry and antisymmetry elements that Dannay *et al.* (1958) first applied to magnetic symmetry. (a) Inversion $\overline{1}$; (b) antiinversion $\overline{1'}$; (c) translation *t*; (d) anti-translation *t'*; (e) rotation 2; (f) anti-rotation 2'; (g) reflection *m*; and (h) anti-reflection *m'*.

ferromagnetic moments have a ferromagnetic component and an antiferromagnetic component.

Collinear antiferromagnetic ordering. An example of collinear antiferromagnetic ordering is shown in Fig. 7.13.16(d). In this case there is only one type of ion (or atom), located in equivalent crystallographic positions and having equal moment amplitudes in an antiparallel orientation.

Canted antiferromagnetic ordering. Fig. 7.13.16(*e*) shows an example of a canted non-collinear antiferromagnetic order in which the moments tilt in such a way that both the \mathbf{M}_x and \mathbf{M}_y directions have antiparallel components. The magnetic unit cell has parameters that are double those of the nuclear unit cell.

A7.13.1.2. The 36 magnetic lattices and 1651 Shubnikov groups

The types of magnetic lattices are shown in Fig. 7.13.17. They are similar to the familiar crystal lattices in that they represent identical chemical entities, but the associated magnetic moments have the same amplitude and opposite orientation. The first row of the figure shows five types of white lattices: P (primitive), C (C-face centred), A (A-face centred), F (all-face centred) and I (body centred). All the white lattices represent ferromagnetic ordering of the moments. A white-and-black (W&B) lattice can be thought of as containing two lattices of the same type, one of which is termed 'white' and the other 'black'. The origin of the black lattice can be located at the centre of a face or at an edge, or at the body centre of the white lattice. For example, Fig. 7.13.17(e) indicates a white I lattice combined with a black Ilattice with origin at c/2 of the white lattice, resulting in the W&B lattice I_c of Fig. 7.13.17(c). The W&B lattices are expressed by two-letter symbols in which the symbol (P, C, A, I or F) of the W lattice is followed by a subscript (A, a, C, c, I or s) which indicates the location of the origin of the black lattice. The capital subscript letters A, C and I indicate that the origin of the B lattice is at the A-face centre (0, b/2, c/2), C-face centre (a/2, b/2, 0) and at the body centre (a/2, b/2, c/2) of the white lattice, respectively. The lower-case subscript letters a and c indicate that the origin of the black lattice is at the centre of the *a* axis (a/2) and *c* axis (c/2)of the white lattice, respectively. For example, the lattice P_C is a combination of a *P* W lattice with a *P* B lattice with the origin at the *C*-face centre $(\frac{1}{2}, \frac{1}{2}, 0)$ of the W lattice, while P_c indicates that the origin of the *P* B lattice is at c/2. These types of magnetic lattices, when applied to the seven crystal systems, give a total of 36 magnetic lattices, of which 14 are pure white and 22 are W&B lattices (see Table 7.13.3).

A7.13.1.3. Magnetic symmetry and antisymmetry operations

Magnetic symmetry elements include all the symmetry elements of the nuclear structure plus the corresponding antisymmetry elements that are produced by adding the time (or current) reversal operation R. Selected typical elements of symmetry and antisymmetry and their symmetry-operation matrices are shown in Fig. 7.13.18. The operation of an element of antisymmetry can be performed as a normal symmetry operation followed by a reversal in direction.

A7.13.1.4. Magnetic reflection conditions for centred lattices

Table 7.13.4 lists the possible neutron magnetic reflection conditions related to the magnetic lattices illustrated in Fig. 7.13.17. The results are obtained by evaluating the neutron magnetic structure factor for $F_{hkl} = 0$ and are confirmed by computations using the program *GSAS* (Larson & Von Dreele, 2004). The conditions for systematic extinctions of magnetic reflections for glide planes and screw axes were reported by Ozerov (1967).

Effects of spin orientation in magnetic structures. Fig. 7.13.3 is a schematic view of the definition of the vectors relevant to the evaluation of the magnetic structure factor. In addition to the magnetic reflection conditions for centred lattices, glides and screws, systematic absences can also be observed when the condition $F_{hkl} = 0$ occurs because the magnetic spin **K** is parallel to the scattering vector $\boldsymbol{\varepsilon}$ for a class of reflections hkl. In this case, the angle α between the scattering and the magnetization vectors is zero and, consequently, $|q| = \sin \alpha = 0$.

Ambiguous spin orientation. Shirane (1959) showed that ambiguous spin structures can be deduced from NPD data, and concluded that: (i) no information can be obtained about the spin

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Table 7.13.4

Integral reflection conditions of centred magnetic lattices corresponding to Fig. 7.13.17

In the symbols for the W&B lattices, the first letter indicates the W lattice (P, C, A, I and F) and the subscript indicates the B lattice.

Type of magnetic lattice and origin for B lattice			Condition for <i>hkl</i> reflection		
W	W&B	Origin of B lattice	W lattices	W&B lattices	
P	P_A P_C P_I P_a P_b P_c, P_s	A-face centre, $(b + c)/2$ C-face centre, $(a + b)/2$ I (body) centre, $(a + b + c)/2$ a-axis centre, $a/2$ b-axis centre, $b/2$ c-axis centre, $c/2$		k + l = 2n + 1 h + k = 2n + 1 h + k + l = 2n + 1 h = 2n + 1 k = 2n + 1 l = 2n + 1	
С	$egin{array}{c} C_A \ C_c \ C_a \end{array}$	A-face centre, $(b + c)/2$ c-axis centre, $c/2$ a-axis centre, $a/2$	h + k = 2n h + k = 2n h + k = 2n h + k = 2n	k + l = 2n + 1 l = 2n + 1 h, k = 2n + 1	
Α	$egin{array}{c} A_C \ A_a \ A_c \end{array}$	C-face centre, $(a + b)/2$ <i>a</i> -axis centre, $a/2$ <i>c</i> -axis centre, $c/2$	k + l = 2n k + l = 2n k + l = 2n k + l = 2n	h + k = 2n + 1 $h = 2n + 1$ $l = 2n + 1$	
Ι	I_c	<i>c</i> -axis centre, <i>c</i> /2	h + k + l = 2n $h + k + l = 2n$	l = 2n + 1	
F	F_s	<i>c</i> -axis centre, <i>c</i> /2	h, k, l all odd or even h, k, l all odd or even	h, k, l all odd	



Chearvad (crosses)

Observed (crosses) and calculated (solid line) intensities of neutron powder diffraction intensity data for the superconductor NaFeAs at 5 K. Possible Bragg positions are shown by vertical lines and the differences between the observed and calculated intensities are shown at the bottom of the figure.

direction if the symmetry is cubic; and (ii) in tetragonal and rhombohedral or hexagonal symmetries, the powder-diffraction intensities can only provide the angle between the spin direction and the unique c axis of the structure.

A7.13.1.5. An example of Rietveld refinement against NPD data for a superconductor

A plot of NPD intensity data for the superconductor NaFeAs (Li *et al.*, 2009) is given in Fig. 7.13.19. The data were measured on the BT-1 high-resolution powder diffractometer at the NIST Center for Neutron Research. A monochromatic neutron beam was produced using a Cu(311) monochromator ($\lambda = 1.5403$ Å) and three collimators with horizontal divergences of 15, 20 and 7'

full width at half-maximum (FWHM) before and after the monochromator, and after the sample. The crystal structure was refined using *GSAS* (Larson & Von Dreele, 2004). The raw data and the data-collection conditions in *GSAS* format are given in the supporting information as files NPD-NCNR_BT1 NaFeAs at 5K.gsas and NCNR-BT1_MonoCu311.inst, respectively. The initial structural model was obtained from the ICSD database (code 165997).

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