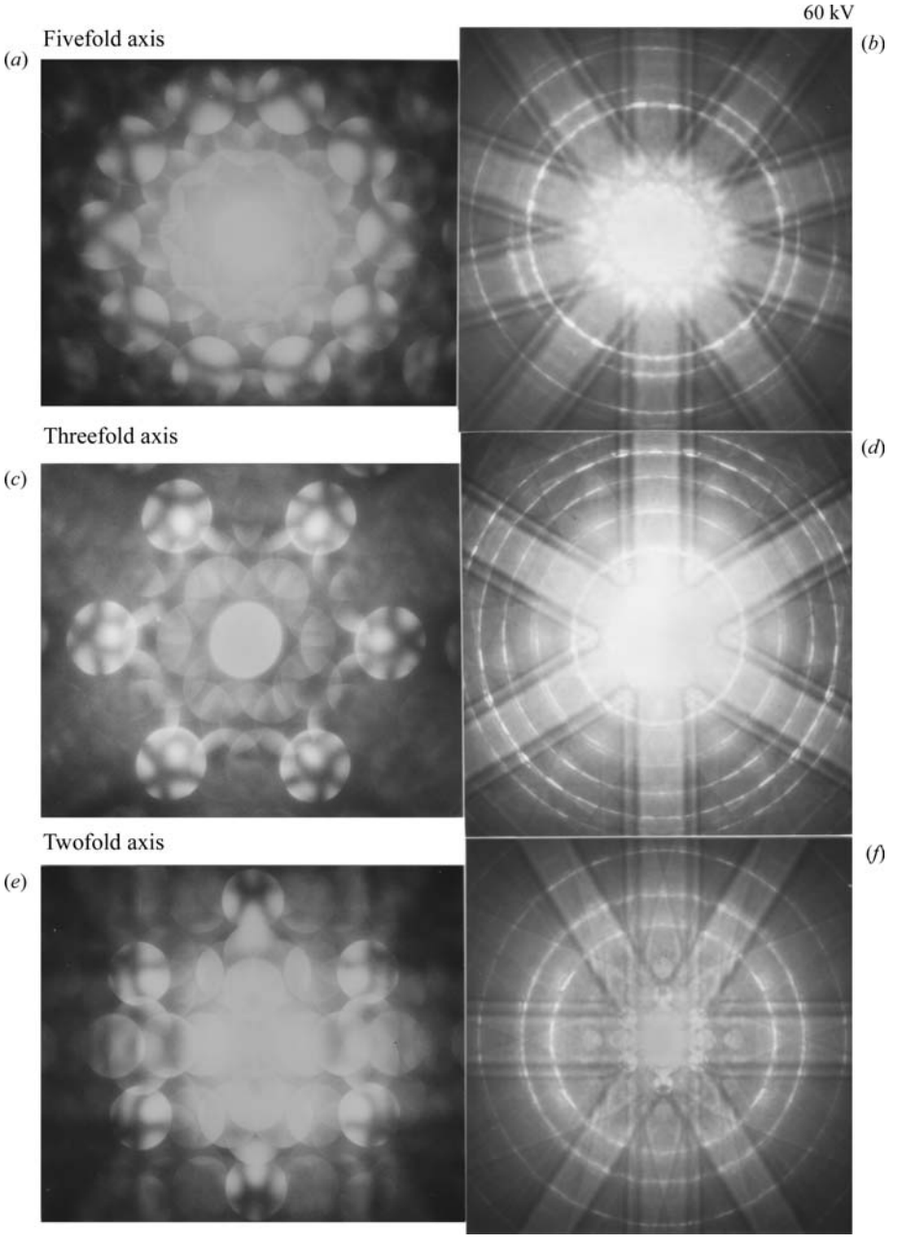

Fig. 2.5.3.24. Three pairs of ZOLZ [(*a*), (*c*) and (*e*)] and HOLZ [(*b*), (*d*) and (*f*)] CBED patterns taken at 60 kV from an area of $Al_{74}Mn_{20}Si_6$ about 3 nm in diameter and about 10 nm thick (Tanaka, Terauchi, Suzuki *et al.*, 1987). Symmetries are (*a*) 10*mm*, (*b*) 5*m*, (*c*) 6*mm*, (*d*) 3*m*, (*e*) 2*mm* and (*f*) 2*mm*.

Fig. 2.5.3.23(*b*) shows a CBED pattern corresponding to Fig. 2.5.3.23(*a*), taken from a specimen area 3 nm in diameter. The excitation errors of two *Umweganregung* paths *a* and *b* are the same at this electron incidence. The reflections 0001, $000\bar{1}$, $200\bar{1}$ and $\bar{2}001$ indicated by white arrowheads show no intensity. Dynamical extinction does not appear as a line in the present case because the width of the extinction line exceeds the disc size of the reflections. Fig. 2.5.3.23(*c*) shows a CBED pattern taken at an incidence slightly tilted toward the b^* axis from that for Fig. 2.5.3.23(*b*) or the [001] zone-axis incidence. The excitation errors are no longer the same for the two *Umweganregung* paths. Thus, it is seen that the kinematically forbidden reflections indicated by white arrowheads have intensities due to incomplete cancellation of waves coming through different paths, which is an additional proof of the dynamical extinction.

2.5.3.5. Symmetry determination of quasicrystals

2.5.3.5.1. Icosahedral quasicrystals

Penrose (1974) demonstrated that a two-dimensional plane can be tiled with thin and fat rhombi to give a pattern with local fivefold rotational symmetries but with no translational symmetry. Mackay (1982) extended the tiling to three dimensions using acute and obtuse rhombohedra, which also resulted in the acquisition of local fivefold rotational symmetries and in a lack of translational symmetry. The three-dimensional space-filling method was later completed by Ogawa (1985). These studies, however, remained a matter of design or geometrical amusement until Shechtman *et al.* (1984) discovered an icosahedral symmetry presumably with long-range structural order in an alloy of Al_6Mn (nominal composition) using electron diffraction. Since then, the term quasicrystalline order, a new class of structural order with no translational symmetry but long-range structural order, has been coined. Levine & Steinhardt (1984) showed that the quasilattice produces sharp diffraction patterns and succeeded in reproducing almost exactly the diffraction pattern obtained by Shechtman *et al.* (1984) using the Fourier transform of a quasi-periodic icosahedral lattice. When analysing X-ray and electron-diffraction data for a quasicrystal, the diffraction peaks can be successfully indexed by six independent vectors pointing to the vertices of an icosahedron. It was then found that the icosahedral quasicrystal can be described in terms of a regular crystal in six

Table 2.5.3.14. *Diffraction groups and CBED symmetries for two icosahedral point groups*

Point group	Diffraction group	BP	WP	DP	±DP
235	$5m_R$	$5m$	5	1	1
					m_R
				m_2	1
	(Projection) $5m1_R$	$10mm$	$5m$	$2 = 1_R$	1
					m_v1_R
				$2m_vm_2$	1
$m\bar{3}\bar{5}$	10_Rmm_R	$10mm$	$5m$	1	2_R
				m_2	2_Rm_2
				m_v	2_Rm_v
	(Projection) $10mm1_R$	$10mm$	$10mm$	2	21_R
				$2m_vm_2$	21_Rm_v

dimensions (*e.g.* Jarić, 1988). A quasicrystal is produced by the intersection of the six-dimensional crystal with an embedded three-dimensional hyperplane (the cut-and-projection technique).

Addition of several per cent of silicon to Al–Mn alloys caused a great increase in the degree of order of the quasicrystal. Bendersky & Kaufman (1986) prepared such a less-strained quasicrystalline $Al_{71}Mn_{23}Si_6$ alloy and determined its point group. They obtained fairly good zone-axis CBED patterns that showed symmetries of $10mm$, $6mm$ and $2mm$ in the ZOLZ discs and $5m$, $3m$ and $2mm$ in HOLZ rings. From these results, they identified the point group to be centrosymmetric $m\bar{3}\bar{5}$. Figs. 2.5.3.24(*a*)–(*f*) show three pairs of CBED patterns taken from an area about 100 nm thick and about 3 nm in diameter of an $Al_{74}Mn_{20}Si_6$ quasicrystal at an accelerating voltage of 60 kV (Tanaka, Terauchi & Sekii, 1987). This quasicrystal was found to have much better ordering than $Al_{71}Mn_{23}Si_6$. The fact that Kikuchi bands are clearly seen in the HOLZ patterns and the profiles of the bands are symmetric with respect to their centre indicates (Figs. 2.5.3.24*b*, *d* and *f*) that the quasicrystal has sufficiently good quality or highly ordered atomic arrangements to perform reliable symmetry determination. Each pair of CBED patterns consists of a ZOLZ pattern and a HOLZ pattern. The former is produced solely by the interaction of ZOLZ reflections, showing distinct symmetries in several discs.

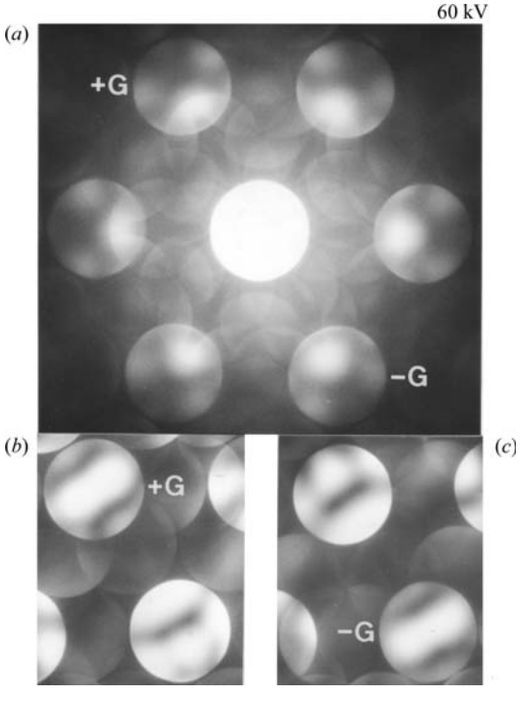

Fig. 2.5.3.25. CBED patterns of $Al_{74}Mn_{20}Si_6$ taken with an electron incidence along the threefold axis. (*a*) Zone-axis pattern showing symmetry $3m$. (*b*,*c*) ±DP showing translational symmetry or 2_R, indicating that the quasicrystal is centrosymmetric.

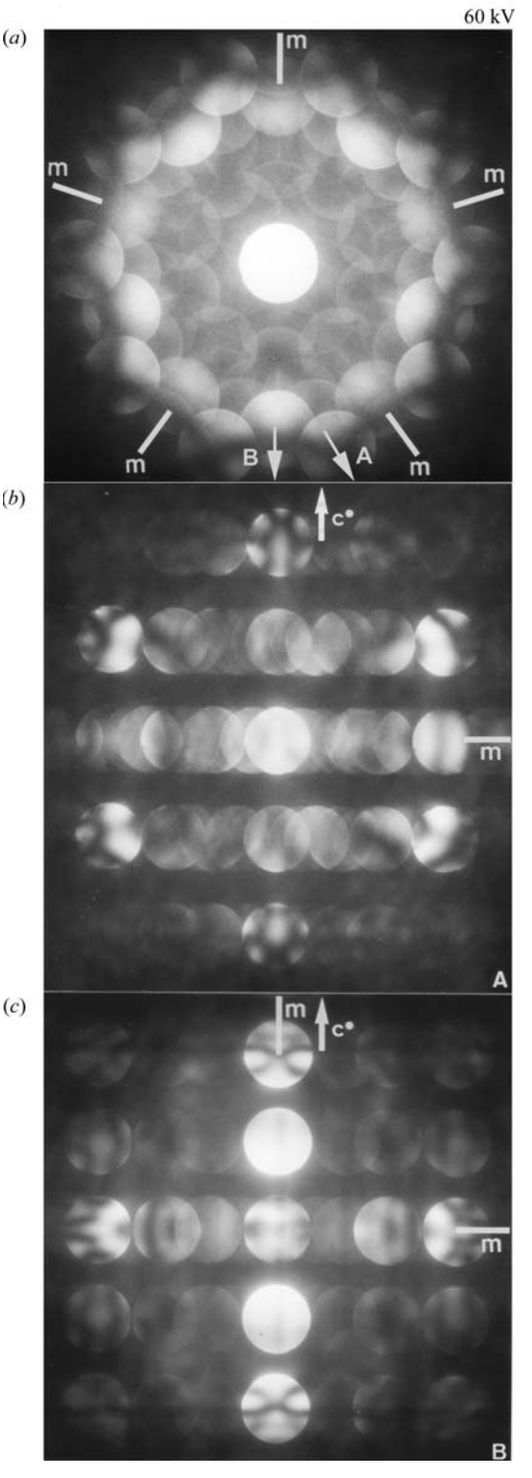

Fig. 2.5.3.26. CBED patterns of metastable $Al_{70}Ni_{15}Fe_{15}$ taken from a 3 nm diameter area. (*a*) Electron incidence along the decagonal axis: symmetry $5m$. (*b*) Electron incidence along direction A indicated in (*a*): symmetry m perpendicular to the decagonal axis. (*c*) Electron incidence along direction B indicated in (*a*): symmetry $2mm$. This alloy is found to be noncentrosymmetric.

The whole pattern of Fig. 2.5.3.24(*a*), formed by ZOLZ reflections, exhibits a tenfold rotation symmetry and two types of mirror symmetry, the resultant symmetry being expressed as

Table 2.5.3.15. *Pentagonal and decagonal point groups constructed by analogy with trigonal and hexagonal point groups*

This table is taken from Saito *et al.* (1992) with the permission of the Japan Society of Applied Physics.

Pentagonal	Decagonal
5	10
–	$\bar{1}0$
$\bar{5}$	10/*m*
5 2	10 2 2
5*m*	10*mm*
–	$\bar{1}0m2$
$\bar{5}m$	10/*mmm*

10*mm*. The whole pattern of Fig. 2.5.3.24(*b*), formed by HOLZ reflections, shows a fivefold rotation symmetry and a type of mirror plane, the resultant symmetry being 5*m*. Figs. 2.5.3.24(*c*) and (*d*) show symmetries 6*mm* and 3*m*, respectively. Figs. 2.5.3.24(*e*) and (*f*) show symmetry 2*mm*. There are two icosahedral point groups, 235 and $m\bar{3}\bar{5}$ (see Table 10.1.4.3 in *IT* A, 2005). The former is noncentrosymmetric with no mirror symmetry but the latter is centrosymmetric. Table 2.5.3.14 shows the diffraction groups expected from these point groups with the incident beam parallel to the fivefold or tenfold axis, and their symmetries appearing in the WP, BP, DP and ±DP. Projection diffraction groups and their symmetries, in which only the interaction between ZOLZ reflections is taken into account, are given in the second row of each pair. Diffraction groups obtained for the other incident-beam directions are omitted because they can be seen in Table 2.5.3.3. The whole-pattern symmetries observed for better-quality images of $Al_{74}Mn_{20}Si_6$ have confirmed the result of Bendersky & Kaufman (1986), *i.e.* the point group $m\bar{3}\bar{5}$. Fig. 2.5.3.25(*a*) shows a zone-axis CBED pattern taken at an electron incidence along the threefold axis. Figs. 2.5.3.25(*b*) and (*c*) show ±DPs taken when tilting the incident beam to excite a low-order strong reflection. The pattern of disc $+G$ agrees with that of disc $-G$ when the former is superposed on the latter with a translation of $-2G$. This symmetry 2_R directly proves that the quasicrystal is centrosymmetric, again confirming the point group as $m\bar{3}\bar{5}$. The lattice type was found to be primitive and no dynamical extinction was observed. Thus, the space group of the alloy was determined to be $Pm\bar{3}\bar{5}$.

Quasicrystals of Al–Mn alloys have been produced by the melt-quenching method and are thermodynamically metastable. Tsai *et al.* (1987) discovered a stable icosahedral phase in $Al_{65}Cu_{20}Fe_{15}$. This alloy has larger grains and is much better quality with less phason strain than $Al_{74}Mn_{20}Si_6$. The discovery of this alloy greatly accelerated the studies of icosahedral quasicrystals. It was found that the lattice type of this phase and of some other Al–Cu–TM (TM = transition metal) alloys is different from that of Al–Mn alloys. That is, Al–Cu–TM alloys display many additional spots in diffraction patterns of twofold rotation symmetry. The patterns were indexed either by all (six) even or all (six) odd, or by a face-centred (*F*) lattice. All the icosahedral quasicrystals known to date belong to the point group $m\bar{3}\bar{5}$; none with the noncentrosymmetric point group 235 have been discovered.

2.5.3.5.2. Decagonal quasicrystals

The first decagonal quasicrystal was found by Bendersky (1985) in an alloy of Al–Mn using the electron-diffraction technique. This phase has periodic order parallel to the tenfold axis, like ordinary crystals, but has quasiperiodic long-range structural order perpendicular to the tenfold axis. The diffraction peaks were indexed by one vector parallel to the tenfold axis and four independent vectors pointing to the vertices of a decagon. Thus, the decagonal quasicrystal is described in terms of a regular crystal in five dimensions.

Two space groups, $P10_5/m$ and $P10_5/mmc$, have been proposed for the alloy by Bendersky (1986) and by Yamamoto & Ishihara (1988), respectively. However, owing to the low quality of the specimens, CBED examination of the alloy could not determine whether the point group is 10/*m* or 10/*mmm*. Furthermore, identification of the space-group symmetry was not possible because observation of dynamical extinction caused by the screw axis and/or the glide plane was difficult. The Al–*M* (*M* = Mn, Fe, Ru, Pt, Pd, ...) quasicrystals found at an early stage were thermodynamically metastable. Subsequently, thermodynamically stable decagonal phases were discovered in the ternary alloys $Al_{65}Cu_{15}Co_{20}$ (Tsai *et al.*, 1989*a*), $Al_{65}Cu_{20}Co_{15}$ (He *et al.*, 1988) and $Al_{70}Ni_{15}Co_{15}$ (Tsai *et al.*, 1989*b*). However, space-group determination was still difficult due to their poor quasicrystallinity.

Tsai *et al.* (1989*c*) succeeded in producing a metastable but good-quality decagonal quasicrystal of $Al_{70}Ni_{15}Fe_{15}$. This alloy was found to be the first decagonal quasicrystal that could tolerate symmetry determination using CBED. The space group was determined to be $P\bar{1}0m2$ by Saito *et al.* (1992).

Fig. 2.5.3.26(*a*) shows a CBED pattern of $Al_{70}Ni_{15}Fe_{15}$ taken with an incidence parallel to the fivefold axis (*c* axis). The pattern clearly exhibits fivefold rotation symmetry and a type of mirror symmetry, the total symmetry being 5*m*. The slowly varying intensity distribution in the discs indicates that the pattern is formed by the interaction between ZOLZ reflections. Thus, the projection approximation should be applied to the analysis of the pattern. Patterns that were related to Fig. 2.5.3.26(*a*) by an inversion were observed when the illuminated specimen area was changed, indicating the existence of inversion domains. Table 2.5.3.15 shows possible pentagonal and decagonal point groups, which are constructed by analogy with the trigonal and hexagonal point groups (Saito *et al.*, 1992).

It can be seen that the point groups that satisfy the observed symmetry 5*m* in the projection approximation are 52, 5*m* and $\bar{1}0m2$. Point group 52 is a possibility because the horizontal