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Icosahedral and decagonal quasicrystals, crystalline phases, and multiple twins in rapidly solidified $Al_{13}Cr_4Si_4$

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Both the icosahedral and decagonal phases have been found in $Al_{13}Cr_4Si_4$ melt-spun ribbons. A definite orientation relationship existing between these two phases is determined by SAD which is the same as that obtained previously by Schaefer and Bendersky. During the icosahedral quasicrystal–crystal transformation in this Al–Cr–Si alloy, the $Al_{13}Cr_4Si_4$ crystalline phase forms at low temperature and an unknown phase at high temperature. Both crystalline phases have definite orientation relationships with the icosahedral phase. The five-fold rotational twins of $Al_{13}Cr_4Si_4$ around the [1 1 0] direction formed from the icosahedral phase follow the group–subgroup relationship. The unknown phase has a hexagonal lattice, $a = 0.73$ and $c = 1.62$ nm.

1. Introduction

In rapidly solidified Al–Cr alloy the existence of the icosahedral phase has been confirmed by Bendersky *et al.* [1] and Bancel and Heiney [2]. The thermal stability and electrical properties of the Al–Cr quasicrystal have been studied by Inoue *et al.* [3]. We have studied the stable crystalline phase, $Al_{45}Cr_7$, and the orientation relationship between the icosahedral and $Al_{45}Cr_7$ phases in detail [4]. The structure of the stable crystalline phase $Al_{45}Cr_7$ is related to the structure of the icosahedral phase by the existence of icosahedra in its complex unit. But until now the decagonal phase has not been observed in the Al–Cr system. According to Bancel and Heiney [2] and Inoue *et al.* [5], the addition of silicon facilitates the formation of quasicrystals. Therefore, we studied the effect of the addition of silicon in the Al–Cr alloy. Although the icosahedral phase in a rapidly quenched specimen of $Al_{62}Cr_{19}Si_{19}$ has been reported by Inoue *et al.* [6], the decagonal phase has not yet been reported in this alloy. We found evidence of the existence of the decagonal phase growing on the surface of the icosahedral phase in melt-spun ribbons of $Al_{13}Cr_4Si_4$ and a definite orientation relationship exists between these two quasicrystalline phases.

The melt-spun $Al_{13}Cr_4Si_4$ ribbons, ~2 mm wide and 30 μm thick, were made in the Institute of Metal Research, Academia Sinica. Thin foils for TEM examination were made from these ribbons by electrolytic thinning in 15% $HClO_4$ in ethanol followed by a brief ion-beam thinning.

2. Icosahedral and decagonal phases in rapidly solidified $Al_{13}Cr_4Si_4$

In melt-spun ribbons of $Al_{13}Cr_4Si_4$ both icosahedral and decagonal phases are found. Fig. 1 shows the morphology of these phases. The decagonal phase, "d", is found to grow as platelets on the surface of the mottled icosahedral phase, "i". Obviously, the "d" platelets have regular growth habit, either parallel to each other or at an angle close to the angle of 63.43° between two five-fold axes of the icosahedral phase. This result is in agreement with the growth model of the Al–Mn decagonal phase suggested by Schaefer and Bendersky [7] that the decagonal phase nucleates on the icosahedral phase with its ten-fold axis along one of the six five-fold directions. The selected-area diffraction (SAD) results are presented below.

Fig. 2 shows the electron diffraction patterns (EDPs) along the main symmetry axes of the icosahedral and decagonal phases. Figs 2a to d are the $\bar{5}$-, $\bar{3}$-, 2- and pseudo 2-fold EDPs of the icosahedral phase and Figs 2a′ to d′ the corresponding pseudo 5-,

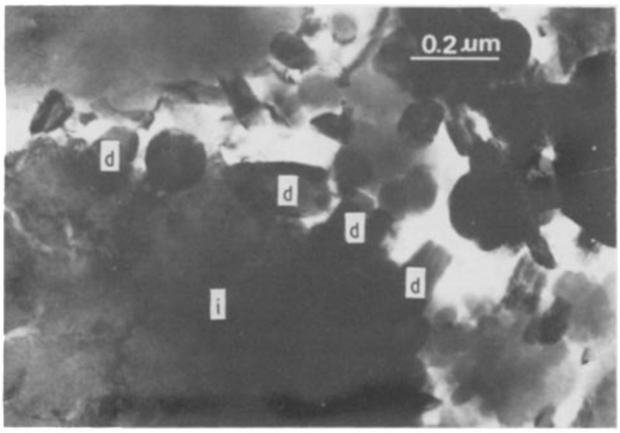

Figure 1 TEM image of the icosahedral and decagonal phases growing together in rapidly solidified $Al_{13}Cr_4Si_4$.

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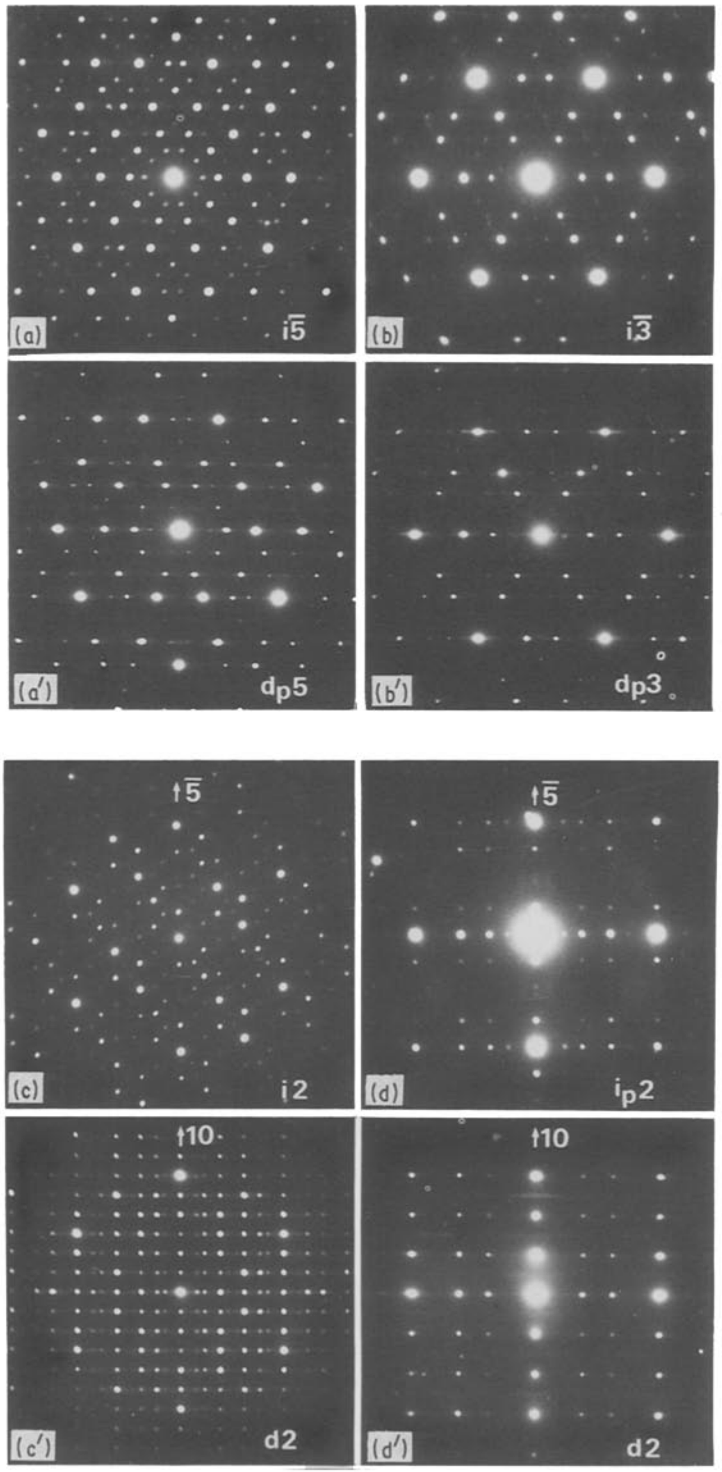

Figure 2 EDPs of the icosahedral and decagonal phases in corresponding pairs: (a to d) $\bar{5}$, $\bar{3}$-, 2- and pseudo 2-fold EDPs of the icosahedral phase; (a′ to d′) pseudo 5-, pseudo 3-, 2(D)-, 2(P)-fold EDPs of the decagonal phase.

pseudo 3- and 2-fold (D and P) EDPs of the decagonal phase. The EDPs are arranged in pairs according to the orientation relationship between these two quasicrystalline phases. The diffuse streaking along the direction perpendicular to the ten-fold direction is obvious in the two-fold diffraction patterns of the decagonal phase (Fig. 2d′). There are six spots between the central and the first bright spot along the periodic ten-fold axis in Fig. 2c′, from this the periodicity is found to be 1.24 nm. Similar diffraction patterns have been obtained earlier in the Al–Mn decagonal phase by Bendersky [8]. However, the periodicity is different (about 1.64 nm) in Al–Fe [9] and Al–Co [10] decagonal phases. This may depend on the structure of the stable crystalline phases.

The orientation relationship between the icosahedral and decagonal phases has been obtained by SAD. Fig. 3a is the composite two-fold pattern of the icosahedral and decagonal phases with the i$\bar{5}$ axis of the former parallel to the d10 axis of the latter. From large-angle tilting experiments the following orientation relationship is obtained:

i$\bar{5}$ ∥ d10, d pseudo5
i$\bar{3}$ ∥ d pseudo3
i2 ∥ d2

This orientation relationship between the icosahedral and decagonal phases is consistent with that obtained by Schaefer and Bendersky in the Al–Mn quasicrystals [7]. Fig. 3b is the superposed pattern of two two-

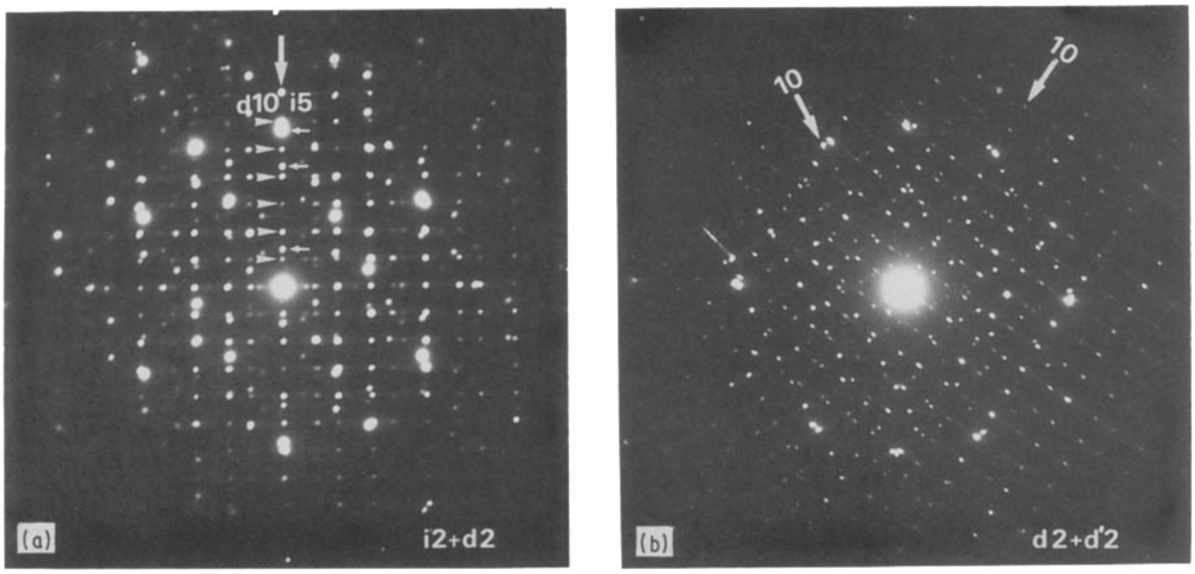

Figure 3 (a) Superposition of the two-fold diffraction patterns of the related icosahedral and decagonal phases. (b) Superposition of the two-fold diffraction patterns of two neighbouring decagonal phases growing on the same icosahedral phase.

fold axis patterns of neighbouring decagonal platelets growing on the same icosahedral grain showing the orientation relation between them. The angle between the two ten-fold axes (periodic array labelled in Fig. 3b) is close to the angle of 63.43° between two $\bar{5}$-fold axes of the icosahedral phase. This verifies further the growth model mentioned above.

The comparison of the compositions of icosahedral and decagonal phases is made qualitatively by the EDAX method. Fig. 4 shows the energy dispersive analysis of X-rays (EDAX) spectra taken from the icosahedral and decagonal phases growing together. It is obvious that the relative silicon content in the decagonal phase is higher than that in the icosahedral phase. Thus it becomes clear that silicon enters and at the same time favours the formation of the decagonal phase.

3. Icosahedral phase and related crystalline phases

In melt-spun ribbons, the $Al_{13}Cr_4Si_4$ crystalline phase has been found together with the icosahedral phase (Fig. 5). The crystalline $Al_{13}Cr_4Si_4$ phase is fcc, $a = 1.0917$ nm, and its space group is F$\bar{4}$3m. The orientation relationship between these two phases is obtained by a detailed analysis of electron diffraction patterns:

$$i\bar{5} \parallel c[1\,1\,0]$$

$$i\bar{3} \parallel c[1\,1\,\bar{1}]$$

$$i2 \parallel c[1\,\bar{1}\,0],\ c[1\,\bar{1}\,1]$$

Fig. 6 is the composite stereographic projection along the [1 1 0] direction of $Al_{13}Cr_4Si_4$ and the five-fold axis of the icosahedral phase. The same orientation relationship has also been found in the case of $NiTi_2$ by Zhang and Kuo [11] and $FeTi_2$ by Dong *et al.* [12]. The crystalline $NiTi_2$ and $FeTi_2$ phases are also fcc (space group Fd$\bar{3}$m), $a = 1.13$ nm. Compared with $Al_{13}Cr_4Si_4$, the lattice parameters are very close and therefore these two phases have similar diffraction patterns. The same orientation relationship may have something to do with the orientation of icosahedra existing in both $FeTi_2$ and $Al_{13}Cr_4Si_4$ phases.

The icosahedral phase exists in both Al–Cr and Al–Cr–Si. According to Cooper [13], in both $Al_{45}Cr_7$ and $Al_{13}Cr_4Si_4$ the chromium atoms are co-ordinated by 12 other atoms lying at the vertices of nearly regular icosahedra. In $Al_{13}Cr_4Si_4$ they form groups of four inter-penetrating icosahedra, each chromium atom

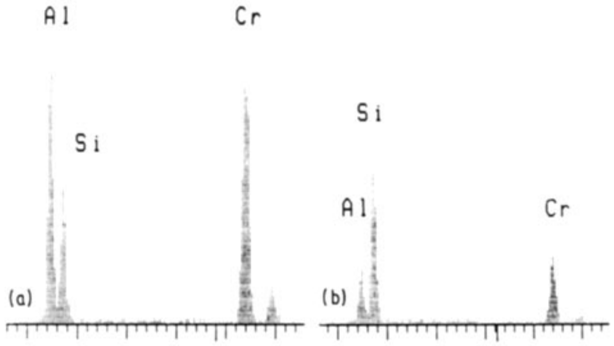

Figure 4 Energy dispersive X-ray spectra of the icosahedral phase (a) and the decagonal phase (b), the latter having a higher silicon content.

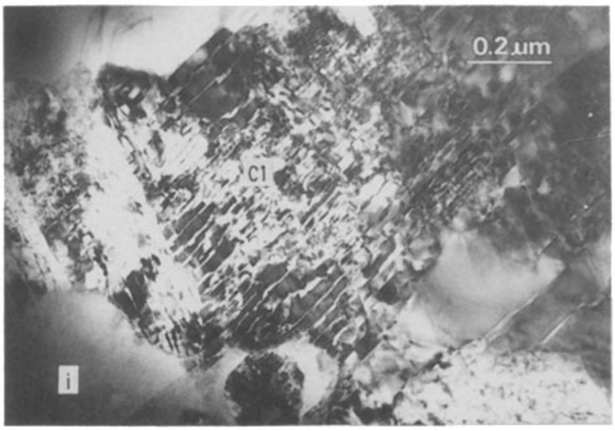

Figure 5 TEM image of the mottled icosahedral phase and the $Al_{13}Cr_4Si_4$ crystalline phase (C1) growing in rapidly solidified Al–Cr–Si alloy.

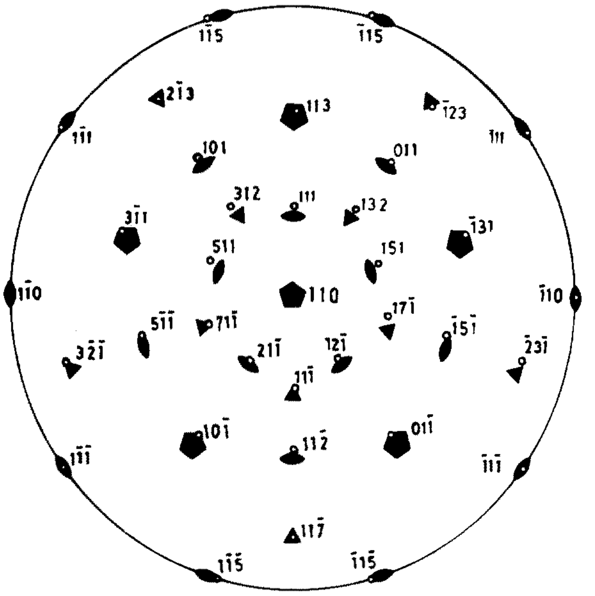

Figure 6 Superposed stereographic projection along the five-fold axis of the icosahedral phase and the [1 1 0] direction of the Al$_{13}$Cr$_4$Si$_4$ crystalline phase showing the orientation relationship between them.

having three chromium neighbours and these groups share corners with other groups. In Al$_{45}$Cr$_7$ these icosahedra are either sharing a vertex, an edge or a triangular face, or interlocked, but many of these icosahedra have the same orientation. This is perhaps the crystallographic basis of the formation of the icosahedral phase during rapid solidification in both Al–Cr and Al–Cr–Si.

Heating experiments have been carried out both *in situ* in an electron microscope and in a vacuum furnace in order to study the transformation of quasicrystals. Fig. 7 shows the morphology of the icosahedral phase after heating to about 500° C. When heating to the crystallization temperature, the Al$_{13}$Cr$_4$Si$_4$ crystalline phase nucleates and grows. On increasing the heating temperature to about 460° C in an electron microscope, the icosahedral phase remaining in the centre of Fig. 7 transforms quickly into another crystalline phase (C2) with a uniform contrast surrounded by Al$_{13}$Cr$_4$Si$_4$ (C1). Obviously this is a diffusion transformation. The longer the heating below the C2 crystallization temperature, the greater the amount of the Al$_{13}$Cr$_4$Si$_4$ crystalline phase. This C2 crystalline phase is an uknown phase not presented in the phase diagram of Al–Cr–Si. By large-angle tilting experiments it is shown that this phase has a hexagonal lattice with $a = 0.73$ and $c = 1.62$ nm. Fig. 8 shows a set of SAD patterns of this hexagonal phase. Fig. 8a is the [0 0 0 1] pattern and the $[2\,\bar{1}\,\bar{1}\,0]$ axis is normal to the [0 0 0 1] axis. By tilting about 30° around the [0 0 0 1] axis, the zone pattern $[2\,\bar{1}\,\bar{1}\,0]$ (Fig. 8b) changes to the $[1\,0\,\bar{1}\,0]$ pattern (Fig. 8c). After tilting by 60°, the same electron diffraction pattern (Fig. 8b) appears again. This is in agreement with a hexagonal crystalline phase.

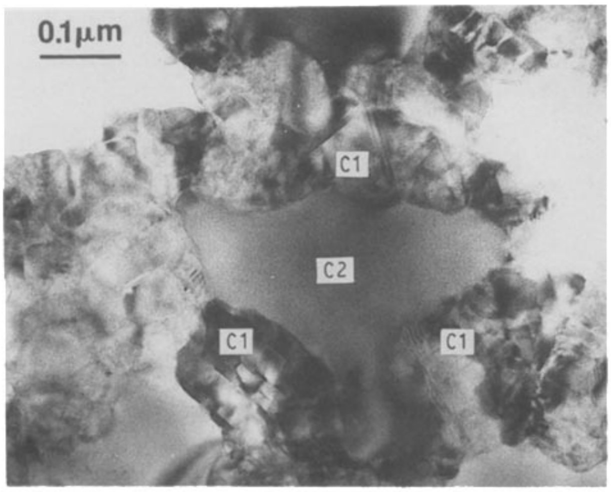

Figure 7 TEM image of the Al$_{13}$Cr$_4$Si$_4$ crystalline phase (C1) and hexagonal phase (C2) transformed from the icosahedral phase after heating to about 500° C.

The orientation relationship between i and C2 phases can be derived from SAD as follows

$$\mathrm{i}\bar{5} \parallel c[2\,\bar{1}\,\bar{1}\,0],\ c[0\,1\,\bar{1}\,0],\ c[\bar{1}\,1\,0\,0]$$

$$\mathrm{i}2 \parallel c[0\,0\,0\,1],\ c[1\,0\,\bar{1}\,0],\ c[\bar{1}\,2\,\bar{1}\,0]$$

In the [0 0 0 1] pattern which superposes the two-fold pattern of the icosahedral phase, the eight spots corresponding to the eight strong spots in the two-fold electron diffraction pattern of the icosahedral phase are marked with arrowheads. Similarly, the ten spots lying on a ring (also marked with arrowheads) corresponding to the ten strong spots in the five-fold electron diffraction pattern can also be found in the $[2\,\bar{1}\,\bar{1}\,0]$ pattern of the icosahedral phase. A further study of this unknown phase would be worthwhile.

4. Multiple twins

During heating, multiple rotation twins of Al$_{13}$Cr$_4$Si$_4$ form easily with the [1 1 0] as the rotation axis. Fig. 9a shows the [1 1 0] pattern of Al$_{13}$Cr$_4$Si$_4$ and Fig. 9b the [1 1 0] pattern of two twins. Successive twinning will give rise to three and four twins as shown in Figs 9c and d, but perfect five-fold twins have not yet been found. This result is very similar to that obtained in Al–Cr [4]. It can be thought that the loss of five-fold symmetry of the icosahedral phase leads to the occurrence of five-fold twins of Al$_{13}$Cr$_4$Si$_4$ when the former transforms to the latter. The angle between $(1\,\bar{1}\,1)$ and $(1\,\bar{1}\,\bar{1})$ is about 72° and this makes it possible to form five-fold rotational twins by successive rotations of 72°. These have been discussed in more detail in the Al–Cr case [4].

5. Conclusions

1. In melt-spun ribbons of the Al$_{13}$Cr$_4$Si$_4$ alloy, both the icosahedral and decagonal phases are found. The decagonal phase often grows on the surface of the icosahedral phase.

2. The orientation relationship between the icosahedral and decagonal phases is

$$\mathrm{i}\bar{5} \parallel \mathrm{d}10, \mathrm{d\ pseudo}5$$

$$\mathrm{i}\bar{3} \parallel \mathrm{d\ pseudo}3$$

$$\mathrm{i}2 \parallel \mathrm{d}2$$

The growth model of the decagonal phase suggested by Schaefer and Bendersky [7] is further verified.

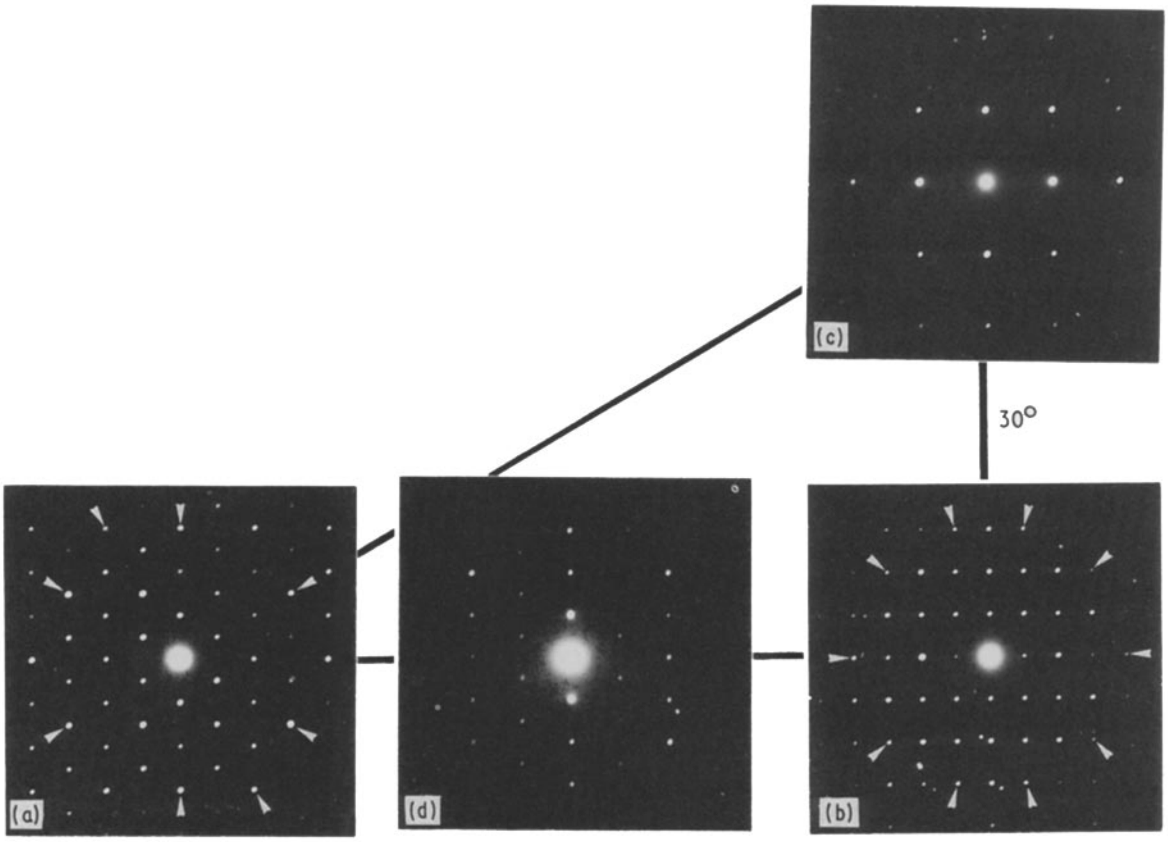

Figure 8 A set of diffraction patterns of the unknown phase C2: (a) [0 0 0 1]; (b) [2 $\bar{1}$ $\bar{1}$ 0]; (c) [1 0 $\bar{1}$ 0] and (d) [2 $\bar{1}$ $\bar{1}$ 3].

3. The icosahedral phase transforms to $Al_{13}Cr_4Si_4$ at low temperature and to an unknown crystalline phase C2 at high temperature.

4. The orientation relationship between the icosahedral phase and $Al_{13}Cr_4Si_4$ crystalline phase is

$$i\bar{5} \parallel c[1\ 1\ 0]$$
$$i\bar{3} \parallel c[1\ 1\ \bar{1}]$$
$$i2 \parallel c[1\ \bar{1}\ 0],\ c[1\ \bar{1}\ 1]$$

This orientation relationship is the same as that obtained in $NiTi_2$ [11] and $FeTi_2$ [12]. Multiple twins around the [1 1 0] axis can easily be found in the transformation of the icosahedral phase to the $Al_{13}Cr_4Si_4$ crystalline phase and can also be explained by the group–subgroup relationship similar to that in the Al–Cr system [4].

5. The unknown phase C2 has a hexagonal lattice with $a = 0.73$ and $c = 1.62$ nm. The orientation relationship between this hexagonal phase and the

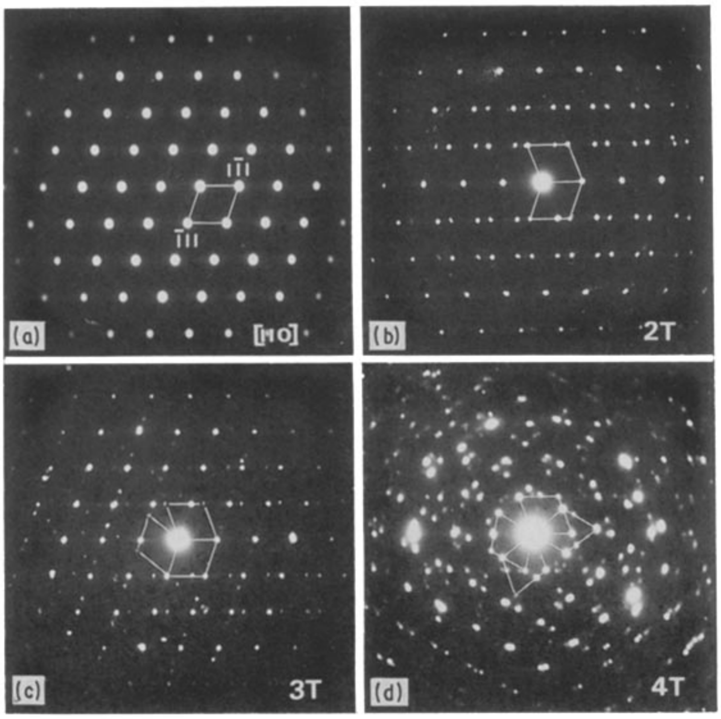

Figure 9 (a) [1 1 0] EDP of the $Al_{13}Cr_4Si_4$ crystalline phase with plane unit cells outlined. (b to d) EDPs of two-, three- and four-fold rotational twins, respectively, along the [1 1 0] axis of $Al_{13}Cr_4Si_4$.

icosahedral phase is

$$\mathrm{i}\bar{5} \parallel c[2\bar{1}\bar{1}0],\ c[01\bar{1}0],\ c[\bar{1}100],$$

$$\mathrm{i}2 \parallel c[0001],\ c[10\bar{1}0],\ c[\bar{1}2\bar{1}0]$$

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