Quasicrystals, crystalline phases, and multiple twins in rapidly solidified Al-Cr alloys

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The crystalline phase coexisting with the icosahedral quasicrystal (point group $m\bar{3}\bar{5}$) in a rapidly solidified Al_7Cr alloy was found to be the monoclinic $Al_{45}Cr_7$ ($2/m$). A definite orientation relationship exists between these two phases which can well be accounted for by the orientation of some of the pseudoicosahedra in $Al_{45}Cr_7$. In addition to the parallel relation of their twofold axes, the [101] and [145] axes of $Al_{45}Cr_7$ are parallel to the $\bar{5}$ and $\bar{3}$ axes, respectively, of the icosahedral phase. Fivefold and threefold rotational twins of $Al_{45}Cr_7$ have been found around these axes; this is discussed from the group-subgroup point of view.

INTRODUCTION

Since the discovery of quasicrystals with icosahedral symmetry in rapidly solidified Al-Cr, Al-Mn, and Al-Fe alloys by Schechtman *et al.*,[1] more than two years ago, a few hundred papers have been published on the nature, metallurgy, crystallography, physical properties, etc., of the Al-Mn quasicrystal. On the contrary, only a few papers concerning the Al-Cr quasicrystal have been reported. The existence of such an icosahedral phase has been further confirmed recently by x-ray,[2,3] electron,[4,5] and neutron[6] diffraction methods. However, the crystalline phase coexisting with this icosahedral phase, either in the as-quenched state or after heating, is still uncertain. Dunlap and Dini[2] found the $Al_{11}Cr_2$ phase after heating to 780 K while Bendersky *et al.*[4] obtained the Al_7Cr phase (in fact, this is really the $Al_{45}Cr_7$ phase[7]). Moreover, no study on the structural relationship between the icosahedral quasicrystal and the crystalline phase in coexistence with it has been made yet.

In a general study of the structural relation between quasicrystals and the crystalline phase with the aim to find new quasicrystals,[8–10] the orientation relationship between the icosahedral quasicrystal and the coexisting crystalline phase in a rapidly solidified Al_7Cr alloy has been determined by transmission electron microscopy (TEM). It has been found that the crystalline phase coexisting with the icosahedral phase is $Al_{45}Cr_7$ which has many pseudoicosahedral units in its monoclinic unit cell, with one of the pseudo $\bar{5}$ axes parallel to [101], which in turn is parallel to the $\bar{5}$ axis of the icosahedral phase. With the reduction of symmetry from $m\bar{3}\bar{5}$ of the quasicrystal to the $2/m$ of the $Al_{45}Cr_7$, many twin variants of the latter may appear when a Al_7Cr quasicrystal is heated to a temperature above the crystallization point. Fivefold twins have been found around the [101] axis exhibiting an electron diffraction pattern (EDP) similar, but not identical, to that of the quasicrystals. Threefold twins have also been found around the [145] axis which is parallel to one of the threefold axes of the quasicrystals.

The experimental facts of such a TEM study are reported in this paper and, in addition, they are correlated with the crystal structure of $Al_{45}Cr_7$. It seems that a close structural relation exists between the icosahedral phase and the $Al_{45}Cr_7$ crystalline phase, and this might be the reason why this quasicrystal can form as a metastable phase during rapid melt-quenching and finally transforms to the equilibrium $Al_{45}Cr_7$ after heating. In order to study the structural relation between these two phases, various projections of the crystal structure and a stereographic projection of [*uvw*] of $Al_{45}Cr_7$ were drawn using the computer program of Dr. Z. Q. Zhou. The melt-spun Al-Cr ribbons, about 2 mm wide and 30 μm thick, with a composition of Al_7Cr, were kindly supplied, in part, by Dr. M. Audier of ENSEEG, Institut National

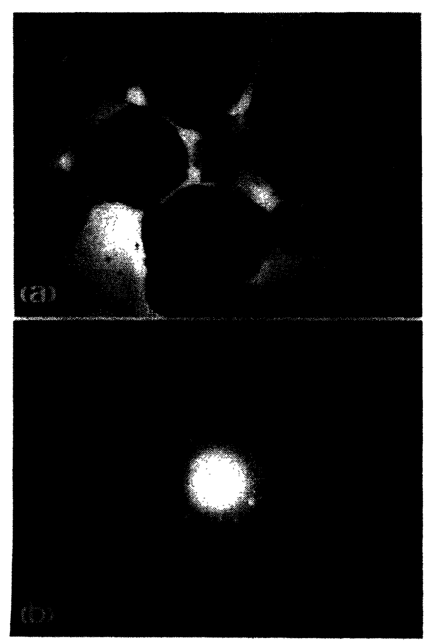

FIG. 1. (a) TEM image of Al-Cr quasicrystals in an amorphous matrix. (b) EDP showing the halos of the amorphous matrix.

FIG. 2. TEM image of tiny $Al_{45}Cr_7$ crystallites formed after heating to 450 °C.

Polytechnique de Grenoble, and partly made in the Institute of Metal Research, Academica Sinica. Thin foils for TEM examinations were made from these ribbons by first electrolytic thinning in 15% $HClO_4$ in ethanol at $-30°$ C, followed by a brief ion beam thinning. The as-quenched specimen was first examined and quasicrystals with a mottled appearance [see Fig. 1(a)] were found in an amorphous matrix, whose presence is verified by the halos in the EDP [Fig. 1(b)]. Some crystalline particles also existed in the spun-quenched ribbon. The typical $\bar{5}$, $\bar{3}$, and 2 fold EDP's of this quasicrystal are shown in Figs. 4(a), 5(a), and 6(a), and the angles among these axes satisfy the icosahedral symmetry. This proves beyond any doubt the presence of the icosahedral phase in this rapidly quenched Al_7Cr alloy, as to be expected from the findings of previous authors. After heating to 450 °C, either *in situ* in an electron microscope or in a tube furnace under vacuum, tiny crystallites were found to occur generally (Fig. 2). This crystalline phase was identified to be $Al_{45}Cr_7$ by selected-area electron diffraction (SAD) using either a Philips EM 420 or a JEM 100CX electron microscope.

CRYSTAL PROJECTIONS OF $Al_{45}Cr_7$

The crystalline phase $Al_{45}Cr_7$ is known to be monoclinic (space group $C2/m$) with $a = 2.5196$, $b = 0.7574$, $c = 1.0949$ nm, and $\beta = 128°43'$.[7] Each unit cell has 104 atoms of which all 14 of the Cr atoms are located at the centers of nearly regular or slightly distorted icosahedra whereas the Al atoms are at their vertices. These icosahedra are either sharing a vertex, an edge, a triangular face or interlocked. In Fig. 3(a), the two interlocked icosahedra (left) appear as a decagon (upper right) when they are projected along the $\bar{5}$ axis. When an icosahedron is projected along the twofold axis, its appearance is shown in the bottom-right diagram in Fig. 3(a).

Figure 3(b) is the projection of the crystal structure of $Al_{45}Cr_7$ along the unique b axis and the a-c planar unit cell is outlined. For clarity the Cr atom is drawn with a somewhat larger dot and this is further enhanced due to

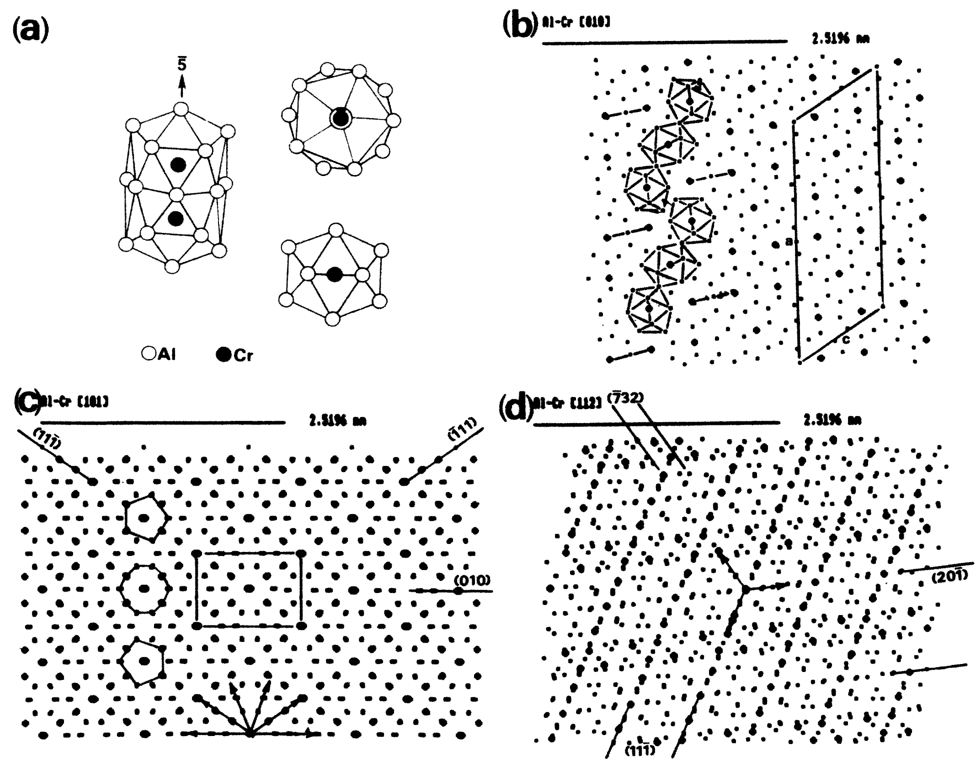

FIG. 3. Crystal structure of $Al_{45}Cr_7$. (a) Icosahedra of different orientations; (b) [010] projection showing $i(2) \| c[010]$ where i and c represent the icosahedral and crystalline phases, respectively; (c) [101] projection showing $i(\bar{5}) \| c[101]$; (d) [112] projection showing $i(\bar{3}) \| c[112]$.

the superposition of the Al atom on it. Comparing with Fig. 3(a), it is obvious that sets of three icosahedra, by sharing vertices, occur in Fig. 3(b). These icosahedra are oriented with one of their twofold axes parallel to the [010] direction of $Al_{45}Cr_7$, though their orientations in the (010) plane are not the same. This is the crystallographic basis of $i(2)\|c[010]$, where i denotes the icosahedral phase and c the $Al_{45}Cr_7$ crystal. The other icosahedra are oriented with their $\bar{5}$ axes close to [010], as evidenced by the deformed ring configuration of ten Al atoms around each Cr atom, and they are linked together in (010) by sharing a triangular face [connected by bars in Fig. 3(b)].

Since there are altogether 15 twofold axes in an icosahedron, it should be possible to find other lattice directions in $Al_{45}Cr_7$ which are also parallel to the twofold axes. Indeed, a large number of icosahedra in $Al_{45}Cr_7$ have one of their twofold directions parallel to the [123] direction and, in addition, these icosahedra are similarly oriented in the plane perpendicular to this direction. Therefore, the [123] EDP resembles very much the twofold EDP of the icosahedral phase [see Fig. 6(d)]. Nevertheless, [010] is still singled out to be the most important direction because it is the only real twofold axis in the $Al_{45}Cr_7$ structure.

Figure 3(c) is the [101] projection of the atoms in $Al_{45}Cr_7$ with the (010), $(\bar{1}11)$, and $(11\bar{1})$ planes indicated. Several points of crystallographic interest can be noted. First, there are many ten-member rings consisting of two pentagons in antisymmetrical positions, as outlined in Fig. 3(c). Evidently they are the icosahedra projected along their $\bar{5}$ axes. Secondly, these ten-member rings are arranged in centered rectangular arrays with an edge ratio close to $\sqrt{2}$, also outlined in Fig. 3(c). This centered rectangular net is rather similar to the (110) lattice plane of a fcc lattice. Thirdly, since the angle between $(11\bar{1})$ and $(1\bar{1}\bar{1})$ is close to 72.0° (about 70.9°), fivefold twins around the [101] direction of $Al_{45}Cr_7$ may occur and this is proved by SAD as shown in Figs. 4(b)–4(f). This apparent fivefold symmetry of the lattice is compatible with the pseudo fivefold point-group symmetry of the slightly deformed icosahedra. Therefore, the [101] projection is as important as the [010] projection in understanding the structural relation between the icosahedral quasicrystal and the crystalline phase. We shall expect $i(5)\|c[101]$. Indeed, the [101] EDP of $Al_{45}Cr_7$ shows ten spots [indexed in Fig. 4(b)] lying close to the second ring of ten strong spots in the $\bar{5}$ EDP of the icosahedral phase shown in Fig. 4(a). This similarity is further enhanced by the presence of multiple twins as shown in Figs. 4(c)–4(f).

Figure 3(d) is the [112] projection of the $Al_{45}Cr_7$ structure and it is of interest for its apparent threefold symmetry. Three families of planes with quite different spacings, indexed in Fig. 3(d), intersect at about 120° with each other. This leads therefore to $i(3)\|c[112]$. Of course, there are other lattice directions of similar nature, such as [145].

FIG. 4. Selected-area electron diffraction patterns (EDP's): (a) $\bar{5}$ EDP of the icosahedral phase; (b) [101] EDP of $Al_{45}Cr_7$ with the centered rectangular cell outlined (similar to the [110] EDP of a fcc crystal) and ten spots indexed [analogous to the ten strong spots in Fig. 4(a)]. The arrow indicates the twofold axis. (c)–(f) [101] EDP's of two-, three-, four-, and fivefold twins (T), respectively, of $Al_{45}Cr_7$. In (f) spots of the $\bar{5}$ EDP of the icosahedral phase are also present.

ORIENTATION RELATIONS

The orientation relationship between the icosahedral phase and $Al_{45}Cr_7$ was studied by means of SAD. Figure 4(b) is the [101] EDP of $Al_{45}Cr_7$, which resembles very much the [110] EDP of a fcc crystal except that the angle between $(1\bar{1}\bar{1})$ and $(11\bar{1})$ is 70.9° rather than 70.5° between two cubic $\{111\}$ planes. There are ten spots more or less evenly distributed rather resembling those of the ten strong spots of the icosahedral phase shown in Fig. 4(a).[11] The indices of these are $\pm(\bar{3}33)$, $\pm(040)$, $\pm(33\bar{3})$, $\pm(51\bar{5})$, and $\pm(5\bar{1}\bar{5})$, and they are nearly of the same distance from the center, though the angle between two neighboring spots may deviate about ±4° from 72°. A successive rotation of this [101] EDP by 71°–72° will bring these spots nearly in coincidence and the final superposed composite EDP of fivefold twins [Fig. 4(f)] appears similar to the $\bar{5}$ EDP of the icosahedral phase shown in Fig. 4(a). This establishes the orientation relation of $i(5)\|c[101]$. A centered rectangular cell was outlined in Fig. 4 which is in fact the reciprocal of the rectangular cell in the [101] projected structure shown in Fig. 3(c).

In several EDP's of $Al_{45}Cr_7$, an apparent threefold symmetry can sometimes be detected, at least as far as the strong spots are concerned. Figures 5(b) and 5(c) are the [112] and [145] EDP's, respectively, and in both of them there are six strong spots lying at about the same position as the hexagon in the $\bar{3}$ EDP of the icosahedral phase [Fig. 5(a)]. This gives $i(3)\|c[112]$ or $c[145]$. In the case of low $[uvw]$ indices such as [112], the number of spots is large, the six strong spots form almost a regular hexagon and they correspond to the three families of planes shown in Fig. 3(d). But in the case of [145] EDP, there are only a few rows of spots and the hexagon of strong spots is somewhat deformed.

Figure 6 presents a comparison of the [010], [110], and [123] EDP's of $Al_{45}Cr_7$ with the twofold EDP of the icosahedral phase. Though the resemblance of Figs. 6(b)

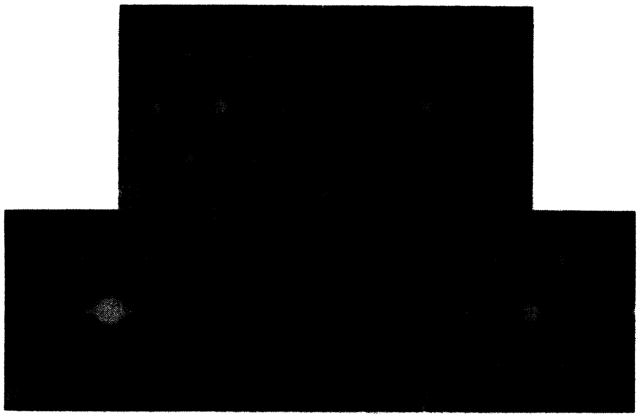

FIG. 5. (a) 3 EDP of the icosahedral phase; (b) [112] EDP of $Al_{45}Cr_7$ with six strong spots indexed; (c) [145] EDP of $Al_{45}Cr_7$ with the arrow head indicating the $[11\bar{1}]^*$. (d),(e) [145] EDP's of 2 and $\bar{3}$ fold twins, respectively, of $Al_{45}Cr_7$ with arrowheads indicating the $[11\bar{1}]^*$ of various twin variants. In (e) spots of the $\bar{3}$ EDP of the icosahedral phase are also present.

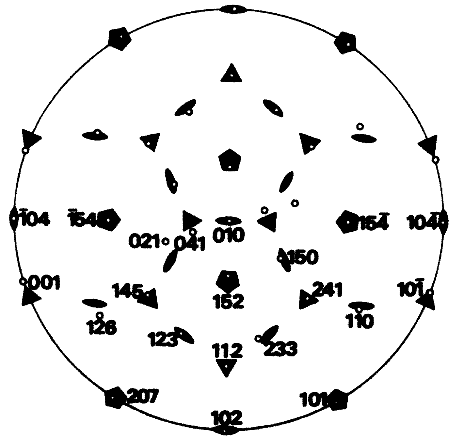

FIG. 7. Stereographic projection of directions of the icosahedral phase (solid shapes) and those of $Al_{45}Cr_7$ (open circles) showing the orientation relationship between them.

and 6(c) to 6(a) is not as obvious as the previous cases shown in Figs. 4 and 5, some similarity can still be traced, such as the six spots marked with arrows. As described above, many icosahedra have their twofold axes parallel to the [010] direction of $Al_{45}Cr_7$, but their orientation on the (010) plane varies and this may perhaps explain the absence of strong spots in the [010] EDP corresponding to those of the icosahedral quasicrystal. As mentioned above, the icosahedra in the [123] projection have almost the same orientation, therefore the [123] EDP shown in Fig. 6(d) looks very similar to the twofold EDP of the icosahedral phase (see the arrowed spots).

Summing up the above findings, the stereographic projection of the [*uvw*] directions of $Al_{45}Cr_7$ is superposed on that of the icosahedral phase (Fig. 7) with

$$i(2) \| c[010] ,$$

$$i(3) \| c[112] ,$$

$$i(5) \| c[101] .$$

Of course, there are also other parallel relations of directions such as $i(3) \| c[001]$ or $c[101]$ and $i(2) \| c[102]$ or $c[104]$ which should also be possibly verified by SAD. However, in the case of directions of high indices, such as $i(5) \| c[152]$, there are only a few rows of spots where no ten-member ring of strong spots can be identified in the [152] EDP.

The good agreement between the experimental orientation relations presented in this section and the crystallographic analysis discussed in the last section may perhaps serve to explain why the icosahedral quasicrystal forms easily in a rapidly solidified Al_7Cr alloy.

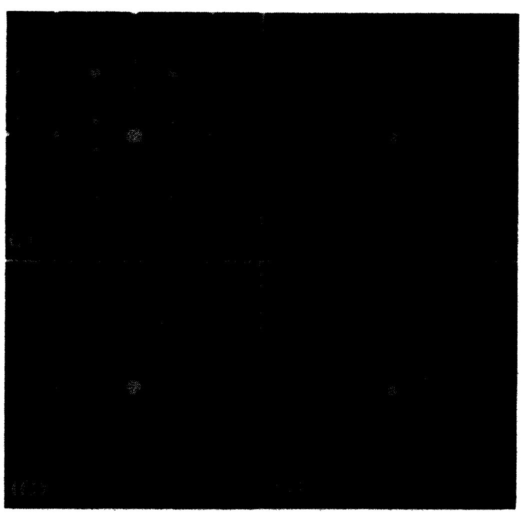

FIG. 6. (a) Twofold EDP of the icosahedral phase; (b)–(d) [010], [110], and [123] EDP's, respectively, of $Al_{45}Cr_7$ with spots similar to the strong spots in (a) marked with arrow heads.

MULTIPLE TWINS

Ordering in alloys is frequently accompanied by a decrease in point-group symmetry, and the symmetry element lost in the ordered crystal structure reappears as the symmetry element among the various twin variants.[12] In other words, the disordered structure and ordered twins have a group-subgroup relationship. This perhaps can also be applied to the quasicrystal-crystal transformation. The point-group symmetry of the icosahedral phase is $m\,\bar{3}\,\bar{5}$ of the order of 120 whereas that of $Al_{45}Cr_7$ is $2/m$ of the order of 4. In other words, if the transformation of the icosahedral phase to $Al_{45}Cr_7$ is considered to be an ordering process, as much as 30 twins variants grouped as fivefold, threefold, and twofold rotational twins should be expected. Obviously, the *b* axis of $Al_{45}Cr_7$ must be parallel to one of the twofold axes of the icosahedral phase.

In fact, fivefold twins of $Al_{45}Cr_7$ have been observed around a lattice direction parallel to one of the fivefold axes of the icosahedral phase. Figures 4(b)–4(f) are the

EDP's of two- three- four-, and fivefold rotational twins, respectively, around the [101] axis. In the successive rotations, the {040} spot will almost superpose in turn with the {333} and {515} spots, and the twofold [010]* axes of these twins are shown with arrows in Fig. 4. It should be pointed out that though Fig. 4(c) looks rather like an EDP of a pair of fcc twins, they are in fact different. First, the first and second horizontal rows are not exactly the same as they should be in the case of fcc twins. Secondly, the spots in the third row do not coincide exactly. The latter is made more obvious when the multiplicity of twins increases as shown in Figs. 4(d)–4(f). The EDP of fivefold twins [5T in Fig. 4(f)] resembles but is not identical to the $\bar{5}$ EDP of the icosahedral quasicrystal, which may serve to show that the icosahedral quasicrystal and fivefold twins are two different types of structures. Both can be present in the same alloy and they need not dispel each other. In other words, the icosahedral quasicrystal is not fivefold twins as postulated by Pauling[13] and others.

A similar case has been found between the Al-Fe decagonal phase ($10/mmm$) and the crystalline phase $Al_{13}Fe_4$ ($m/2$, $\beta = 107.71°$).[10] The orientation relation is now $i(10) \| c[010]$ and this is not unexpected at all. The twofold axis of $Al_{13}Fe_4$ can easily be accommodated in the tenfold axis of the decagonal phase and the symmetry elements that disappeared during this transformation, $5m$, will reappear among the ten twin variants. In fact, ten-fold twins have been found with a common [010] axis and the angle between two neighboring twin variants is 36°, which is just about one half of (π-β).

Threefold rotational twins have also been found around the [145] direction of $Al_{45}Cr_7$. Comparing Figs. 5(c) and 5(d), the rotation of about 120° of a pair of twins is obvious (shown with arrow heads) and the strong spots do not coincide. Again, the EDP of threefold twins [Fig. 5(e)] is similar but not identical to the $\bar{3}$ EDP of the icosahedral phase.

It has been made clear from the results presented, that the group-subgroup relation can be equally well applied to the quasicrystal-twins transformation, and this is important because a noncrystallographic point group is now involved.

CONCLUSIONS

The following conclusions are drawn.

(1) The icosahedral quasicrystal in an amorphous matrix has been obtained in the melt-spun ribbons of an $Al_{45}Cr_7$ alloy. After heating to 450° C, many small crystallites of $Al_{45}Cr_7$ appeared in coexistence with the icosahedral phase. No $Al_{11}Cr_2$ has been detected.

(2) In this monoclinic $Al_{45}Cr_7$ structure all Cr atoms are located at the centers of slightly deformed icosahedra. Various projections of this structure have been drawn and it was shown that some icosahedra have one of their twofold axes parallel to [010], one of their pseudo $\bar{5}$ axes to [101], and one of their pseudo $\bar{3}$ axes to [112] or [145] of $Al_{45}Cr_7$.

(3) A definite orientation relationship exists between the icosahedral quasicrystal (point group $m\,\bar{3}\,\bar{5}$) and the crystalline $Al_{45}Cr_7$ ($2/m$) phase:

$$i(2) \| c[010] ,$$

$$i(3) \| c[112] \text{ or } c[145] ,$$

$$i(5) \| c[101] .$$

The first one is dictated by the fact that a monoclinic crystal can only be accommodated in an icosahedral quasicrystal with its b axis parallel to one of the twofold directions of the latter.

(4) After heating the quasicrystal to 450 °C, twins of $Al_{45}Cr_7$ occur abundantly with their [010] direction parallel to one of the twofold directions of the icosahedral phase. Therefore, fivefold and threefold twins were found around the [101] and [145] axes, respectively, of $Al_{45}Cr_7$. This can be understood from the group-subgroup relation of the structures of these two phases, $m\,\bar{3}\,\bar{5}$ and $2/m$ respectively. The symmetry element lost in the parent structure during the ordering transformation reappears between the twin variants of the transformed structure. Such a relation occurring in a noncrystallographic point group is of both theoretical and practical interest.

(5) From the pseudoicosahedral units in the crystal structure of $Al_{45}Cr_7$ and the orientation relationship between the icosahedral phase and $Al_{45}Cr_7$, as well as the fivefold twin variants of $Al_{45}Cr_7$ in conclusions (2)–(4), it seems that the crystalline and quasicrystalline phases in Al_7Cr are linked by the icosahedra in them and this may explain why the icosahedral quasicrystal forms easily in this alloy after solidification.

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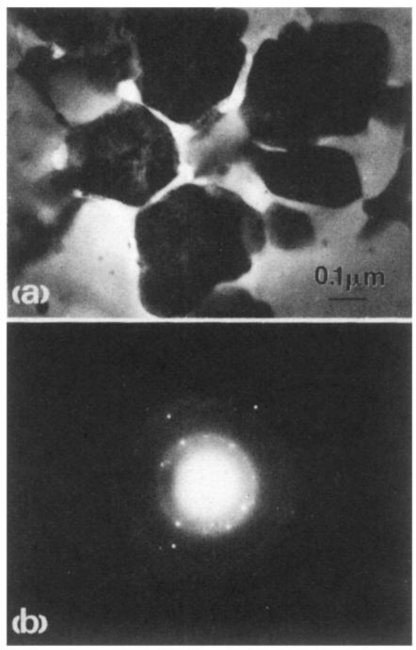

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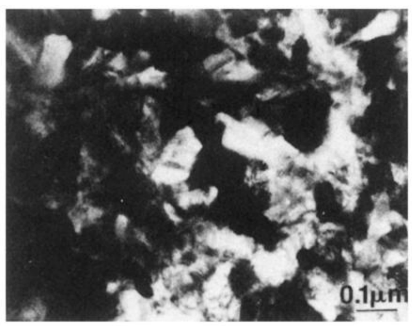

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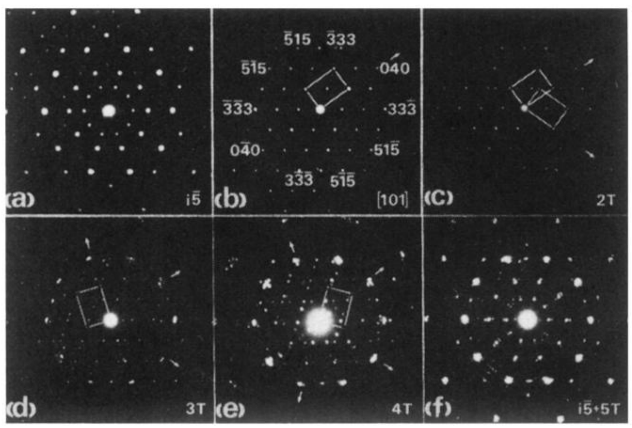

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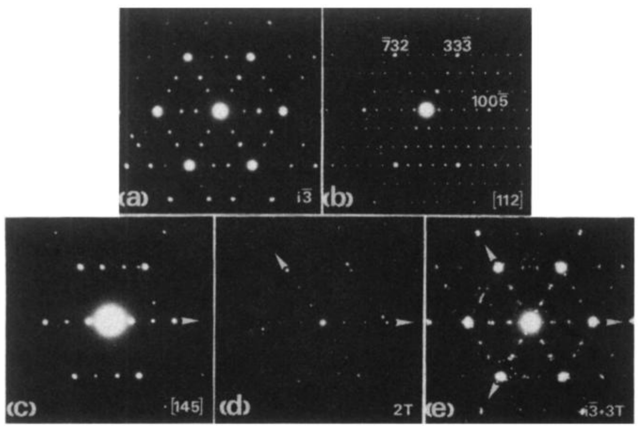
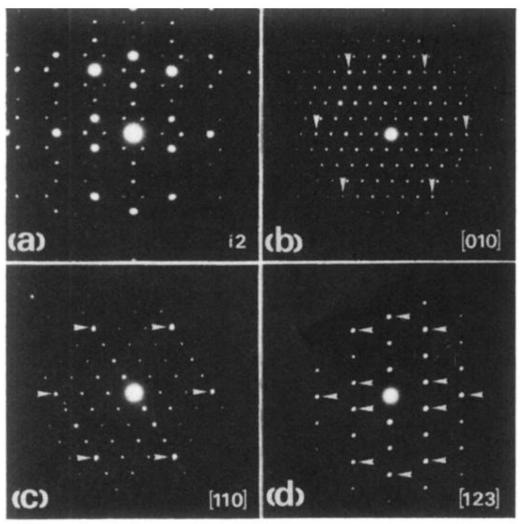


FIG. 5. (a) 3 EDP of the icosahedral phase; (b) [112] EDP of $Al_{45}Cr_7$ with six strong spots indexed; (c) [145] EDP of $Al_{45}Cr_7$ with the arrow head indicating the $[11\bar{1}]^*$. (d),(e) [145] EDP's of 2 and $\bar{3}$ fold twins, respectively, of $Al_{45}Cr_7$ with arrowheads indicating the $[11\bar{1}]^*$ of various twin variants. In (e) spots of the $\bar{3}$ EDP of the icosahedral phase are also present.



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