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# Two-dimensional pentagon quasicrystal in an Al–Co–Ni–Tb alloy obtained by quenching under high static pressure

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A transmission electron microscopy study of quasicrystals was carried out in Al–Co–Ni–Tb alloy which was obtained by quenching under high static pressure and a new two-dimensional pentagonal quasicrystal was discovered. An unique five-fold axis is observed in its diffraction patterns and the periodicity along the five-fold axis is 0.4 nm. Another feature of the pentagonal phase is that no extinction exists in the diffraction patterns along the direction perpendicular to the five-fold axis. A comparison of the high resolution electron microscopy images of the pentagonal phase and the decagonal quasicrystal is given. The effect of high pressure is discussed.

## 1. Introduction

Since Shechtman *et al.* first reported the icosahedral quasicrystal [1] with five-fold symmetry, the study of quasicrystals has been attracting scientists' attention. Afterwards, decagonal (ten-fold) [2], eight-fold [3] and twelve-fold [4] quasicrystals were also discovered. The former is a three-dimensional quasicrystal, while the latter three are two-dimensional ones. The decagonal quasicrystal is quasiperiodic in two-dimensions and periodic in the third, which is parallel to the ten-fold axis. Recently, Saito *et al.* [5] determined the space group of decagonal quasicrystals of an $Al_{70}Ni_{15}Fe_{15}$ alloy as $P\overline{10}m2$ using convergent beam electron diffraction.

The discovery of a stable decagonal quasicrystal in Al–Co–Ni [6] makes this system more attractive, and subsequently a large volume of work has been carried out on Al–Co–Ni alloys [7–9]. Besides decagonal quasicrystals, crystalline approximants were also found [7].

Since the Al-rich Al–$M$ ($M$ = transition element metals) intermetallic compounds consist mainly of icosahedral clusters, quasicrystals can be obtained in most Al–$M$ systems. It is well known that transition metals have some unfilled $d$ orbits. Taking into account that rare earth elements have some unfilled $f$ orbits and nearly unoccupied $d$ orbits, they not only have some similar properties to transition metals, but also their own special properties. A small amount of the rare earth element Tb was doped into some alloys in the prospect of obtaining some new metastable intermediate phases resulting from it; it was hoped that the rare earth Tb could provide some centres of non-translational order symmetry and affect the crystalline environment and intermediate states.

In preparing quasicrystals, several techniques have been reported. In this experiment, the authors used the method of quenching from the fusion state under high static pressure (MQFHSP). The use of high pressure will restrict the motion of atoms; cooling under high pressure equivalently equals to an increment of the cooling rate at atmospheric pressure, and therefore the cooling rate under high pressure is in fact faster than that under normal pressure [10, 11], so some intermediate metastable phases are favourable to intercept and capture due to the high pressure.

Studies of phase formation in the Al–Co–Ni–Tb alloy obtained by MQFHSP have been carried out by the authors. Six orthorhombic phases, $C_1$–$C_6$, with giant unit cells, were found in the $Al_{70}Co_{15}Ni_{10}Tb_5$ alloy, which are considered as new crystalline approximants of the decagonal quasicrystal [12, 13]

In this paper is reported the discovery of a new pentagonal phase in Al–Co–Ni–Tb alloy, which is a two-dimensional quasicrystal with a unique five-fold axis perpendicular to a quasiperiodic plane and parallel to a periodic axis.

## 2. Experimental procedure

An alloy of the composition $Al_{70}Co_{15}Ni_{10}Tb_5$ was prepared by melting high purity metals in an arc furnace under an argon atmosphere. Ingots of the alloy were crushed into powder and sealed in a tube for high static pressure and subsequently treated by MQFHSP at 7.0 GPa. The powdered sample was

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heated to the fused state above 1700 °C for 3 min and then quenched at a cooling rate of about $10^2$–$10^3$ °C $s^{-1}$. The ingot was cut into slices from which thin foil specimens for transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) were prepared by grinding and subsequent ion milling. The high pressure equipment used in the experiment was a 19.6 MN press. TEM and HREM experiments were carried out on Philips EM-420 and CM-12 electron microscopes, respectively, each equipped with a large angle ($\pm 30$ and $\pm 60°$) double-tilting goniometer through which electron diffraction patterns of main zone axes are easy to obtain successively from a single grain.

## 3. Results and discussion

Fig. 1 shows the selected area electron diffraction (SAED) patterns from the new phase in the Al–Co–Ni–Tb alloy. The distribution of the diffraction spots in Fig. 1a resembles a ten-fold SAED pattern of a decagonal quasicrystal, in which these spots do not lie on a periodic cross grid but on a quasiperiodic one. However, an obvious five-fold symmetry is noticed in this pattern, see the spots marked with arrows. Experiments of electron diffraction by tilting the sample with large angles show that this is the unique five-fold axis in the structure of the new phase.

Two SAED patterns perpendicular to the five-fold axis are also shown in Fig. 1b, c, all spots in these patterns are located on an equally spaced straight line and the five-fold axis in the periodic direction which means a two-dimensional quasicrystal. Reflection arrays originating from the quasiperiodicity are seen in directions perpendicular to the five-fold axis.

Unlike the decagonal quasicrystal in which there are extinctions in the $2P$ diffraction patterns (one kind of two-fold electron diffraction pattern of decagonal quasicrystal) due to the existence of a $10_5$ screw axis, no extinction is observed in the pentagonal quasicrystal (see Fig. 1c). In other words, diffraction spots appear at positions corresponding to $\pm 0.4$ nm in the five-fold direction in Fig. 1c without any extinction. This is in accordance with the existence of a five-fold axis in the pentagonal quasicrystal. This point will be discussed later. As in [5], diffraction spot arrays at the $X$ positions [$(0.8/n)$ nm; $n$; even] in Fig. 1c are explained by the quasiperiodicity of the atomic arrangement. Besides this, it is found that diffraction spots also appear at the $Y$ positions [$(0.8/n)$ nm; $n$; odd]. Those at the $Y$ positions are not attributed to any periodicity, nor to quasiperiodicity. The presence of arrays at $Y$ is possibly due to structural modulations with wave number vectors $\boldsymbol{K}$ and $\boldsymbol{K}'$, as shown in Fig. 1c. A pair of reflection spots at $Y$ appearing on both sides of $X$ can be considered to be satellites connected by the wave vector $\boldsymbol{K}$ or $\boldsymbol{K}'$ with a fundamental reflection on the $X$. Another possible explanation is that the spots labelled $Y$ were produced by double diffraction. They could possibly be due to a second phase, such as some kind of surface oxide layer. These explanations indicate that periodicity in the five-fold direction is 0.4 nm and that all the fundamental reflections exist in both kinds of two-fold electron diffraction patterns (EDPs) Fig. 1b, c.

Fig. 2 is a microEDP of the pentagonal quasicrystal along the five-fold direction. Obviously, there are five strong spots in it and it shows nearly five-fold symmetry; it indicates again that the phase described above is a pentagonal quasicrystal.

Generally, a five-fold axis in real space is shown as ten-fold symmetry in its electron diffraction pattern and this is true for the EDP of five-fold axes of icosahedral quasicrystals. The appearance of real five-fold symmetry in the EDP in Fig. 1a is explained as a strong dynamical diffraction effect, since a relatively thick region is used in the TEM experiments.

Fig. 3 is a lattice image of the pentagonal quasicrystal, taken with the incident beam parallel to the pentagonal symmetry axis, corresponding to the EDP in Fig. 1a. The electron diffraction spots, whose distances from the centre spot are shorter than those of the spots at the end of the arrows marked in Fig. 1a, were allowed through the objective aperture. Although the resolution of the image is not so high since the region is relatively thick, the structural characteristics of the

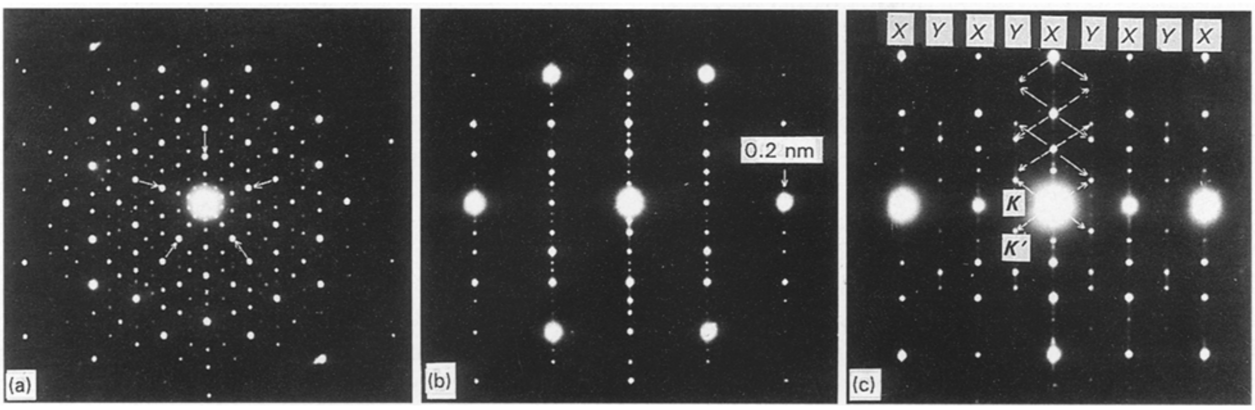


*Figure 1* The selected area electron diffraction patterns of the pentagonal phase: (a) The EDP of the pentagonal axis, the electron diffraction spots show five-fold symmetry and is quasiperiodic in the two-dimensional plane. (b, c) The EDPs obtained by successive rotation of 18° around the pentagonal axis. Reflections appearing at lines denoted by $Y$ are explained by neither a periodic structure nor a quasiperiodic one. A possible explanation is to regard the reflections as satellites due to modulated structures with modulation wave vectors $\boldsymbol{K}$ and $\boldsymbol{K}'$ shown in Fig. 1c.

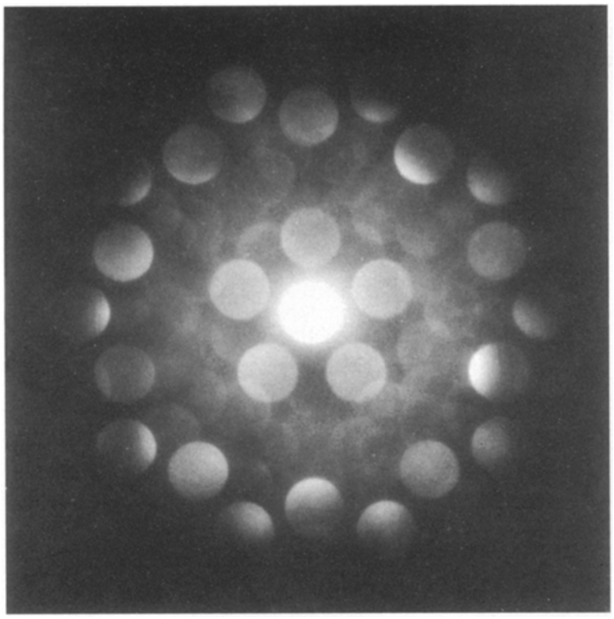

*Figure 2* MicroEDP of pentagonal phase. The incident beam is parallel to the unique pentagonal axis. The diffraction spots show nearly five-fold symmetry.

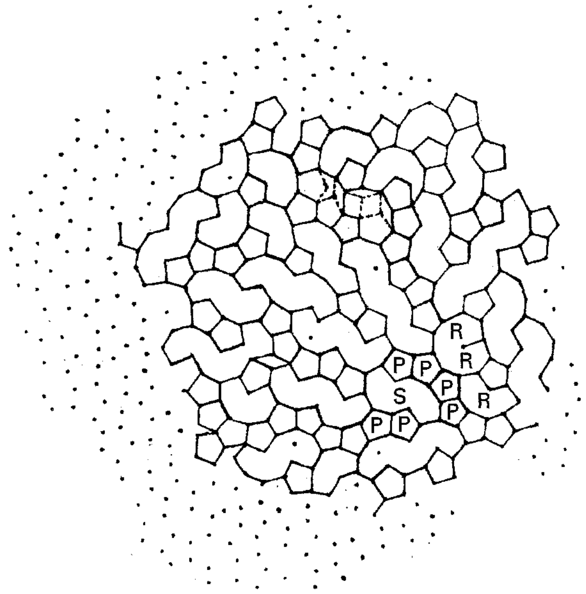

*Figure 4* Schematical illustration of tiling constructed by the connection of bright dots in the lattice image. It is mostly composed of pentagonal units (P) and some large units (R and S) which can be divided into pentagons and rhombs/boats.

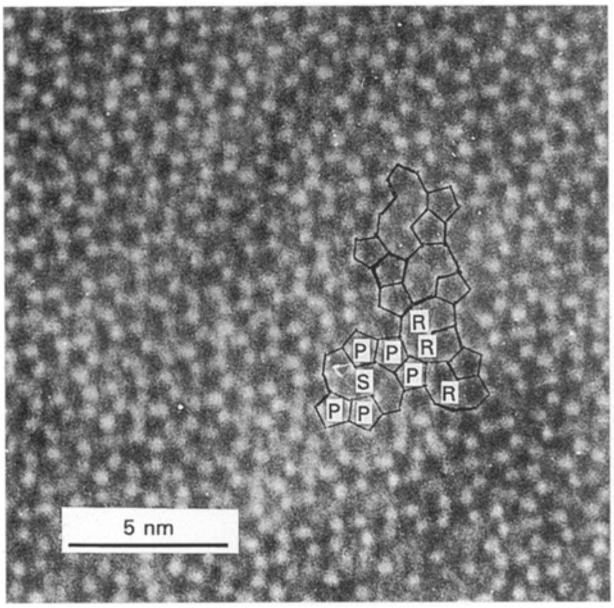


*Figure 3* The lattice image of the pentagonal quasicrystal.

pentagonal quasicrystal can also be observed. Schematical illustration of tiling, constructed by connection of the bright dots in the lattice image, is shown in Fig. 4. It is shown that the tiling is mostly composed of pentagonal units (marked P in Fig. 4) and some large units (marked R and S, S is the overlap of two Rs) which can be divided into pentagons and rhombs or boats (outlined with dotted lines). It is worth noticing that the pentagons always connect in a short chain and never form circles, which are related to the trace of tenfold symmetry, so the lattice image agrees with the five-fold EDP shown in Fig. 1a.

Penrose tiling is considered as a successful geometric model of the decagonal quasicrystal; in fact, it is more suitable for the case of the pentagonal phase. Penrose tiling is a quasiperiodic pattern with five-fold symmetry and is composed of two kinds of rhombs. A simple model can be produced by assuming atoms on the vertex of the Penrose tiling and packing these layers with a $10_5$ screw axis. Such a model can explain most features of decagonal quasicrystals. A simple model of pentagonal quasicrystals can then be explained by packing the Penrose tiling without a $10_5$ screw axis. So it is understood that the existence of pentagonal quasicrystals is not surprising.

Recently, Saito *et al.* [5] reported a new kind of $Al_{70}Ni_{15}Fe_{15}$ decagonal quasicrystal with periodicity of 0.4 nm and determined the space group as a non-centrosymmetric $P\overline{10}m2$ by the convergent beam electron diffraction method. Their experimental results are closely related to those of the authors in $Al_{70}Co_{15}Ni_{10}Tb_5$ alloy,

1. both phases appear to have five-fold symmetry in their EDPs along a ten-fold (five-fold) axis when strong dynamical effects exist,
2. both phases show no extinction in diffraction patterns perpendicular to the unique ten-fold (five-fold) axis, and
3. both phases have a periodicity of 0.4 nm.

A most important point is that the $\overline{10}$ symmetry element is identical to $5/m$, and then the space group $P\overline{10}m2$ can be also written as $P5/mm2$. Quasicrystals with point group $10/mmm$ or $10/m$ are nominated as decagonal phases [8], therefore quasicrystals with point group $5/mm2$ or $5/m$ are more reasonable to be nominated as pentagonal phases. In the authors' point of view, both $Al_{70}Co_{15}Ni_{10}Tb_5$ and $Al_{70}Ni_{15}Fe_{15}$ [5] quasicrystals belong to pentagonal phases.

## 4. Conclusions

Electron diffraction patterns show clearly that there is a unique five-fold axis perpendicular to a quasiperiodic two-dimensional array, and that there are no extinction rules in the EDPs which are perpendicular to the unique non-crystallographic axis in the pentagonal phase. HREM images of the pentagonal phase are mostly composed of pentagonal units and some large units which can be divided into pentagons and rhombs or boats; however, the pentagons never form circular chains which show the trace of ten-fold symmetry. Based on a global crystallographic analysis, one refers to the pentagonal phase as a kind of two-dimensional quasicrystal with five-fold rotational symmetry.

The addition of the rare-earth element Tb into the Al–Co–Ni alloy system produces a pentagonal phase in the alloy $Al_{70}Co_{15}Ni_{10}Tb_5$ prepared by the MQFHSP method. By the MQFHSP method, only at a much lower cooling rate ($10^2$–$10^3$ °C $s^{-1}$), are some metastable phases [12, 13], including twelve-fold quasicrystals [14] easy to obtain. These metastable phases are normally obtained at a much higher cooling rate ($10^5$–$10^8$ °C $s^{-1}$) or are difficult to obtain under normal pressures and high temperatures, e.g. during rapid solidification. Thus MQFHSP is an excellent technique for studying quasicrystals and other metastable intermediate phases.


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