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Formation of Decagonal Quasicrystal in the Al–Pd–Mn System and Its Structure

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Formation of a decagonal quasicrystal in $Al_{70}Pd_{30-x}Mn_x$ alloys (x=8–20) and its structure were examined by X-ray powder diffraction, electron diffraction and high-resolution electron microscopy. The decagonal quasicrystal is formed as a coexisting phase with an icosahedral phase in the composition range of x=10–15, and as a single phase at a composition of x about 20. The structure of the decagonal phase is a mixture of decagonal quasicrystalline regions with some linear phason strain and microcrystalline regions. We propose that the structure of Al–Pd–Mn decagonal quasicrystal may be interpreted as a tiling formed by atom cluster linkages, which are different to those reported in Al–Ni–Co and Al–Cu–Co decagonal quasicrystals.

KEYWORDS: decagonal quasicrystal, quasicrystal, high-resolution electron microscopy, X-ray diffraction, Al–Pd–Mn

§1. Introduction

Since the discoveries of stable decagonal quasicrystals in conventionally solidified Al–Cu–Co and Al–Ni–Co alloys,[1-3] many experimental studies to clarify atomic arrangements of the decagonal quasicrystals have been made by high-resolution electron microscopy,[4-8] X-ray diffraction[9] and scanning tunneling microscopy.[10] Almost all of these studies show that structures of the decagonal quasicrystals may be interpreted in terms of tilings of some atom clusters. In our previous papers,[6-8] it was found that a highly ordered decagonal quasicrystal, formed as a high temperature phase in the Al–Ni–Co and Al–Cu–Co alloys, shows a pentagonal tiling of atom clusters with some random phason strain, and that it undergoes a structural change to rhombic tilings at low temperatures. Recently, Beeli *et al.*[11] reported that a stable decagonal quasicrystal is formed in the Al–Pd–Mn system at a composition adjacent to the stable icosahedral phase, which was first found by Tsai *et al.*[12] Our intention in the present work is two-fold; the first is to study formation of the Al–Pd–Mn decagonal quasicrystal, and the second is to investigate its structure as a tiling of atom clusters.

§2. Experimental Procedures

Some alloy ingots with nominal compositions $Al_{70}Pd_{30-x}Mn_x$ (x=8–20) were prepared by melting mixtures of pure Al, Pd and Mn metals in an arc furnace in an argon atmosphere. Parts of the products were sealed in evacuated quartz tubes and various heat treatments were made. Thin samples for electron microscopy were prepared by dispersing crushed materials on holey carbon films. Electron diffraction patterns and high-resolution images were obtained on a 400 kV electron microscope (JEM-4000EX) with a resolution of 0.17 nm.

§3. Experimental Results

3.1 *Formation of decagonal quasicrystal*

Figure 1 shows X-ray diffraction patterns of the $Al_{70}Pd_{30-x}Mn_x$ alloys (x=8–20) as-cast, together with those annealed at 800°C for 16 hrs and then quenched in water. We also carried out X-ray diffraction analysis of samples which were slowly cooled after annealing at 800°C and their diffraction patterns are nearly the same as those of the quenched samples. All peaks in the diffraction pattern of the annealed $Al_{70}Pd_{22}Mn_8$ sample (x=8, (b)) were indexed as an icosahedral quasicrystal phase. Peaks of the decagonal phase, indicated with small arrows, first appear in the annealed $Al_{70}Pd_{20}Mn_{10}$ alloy (x=10, (b)) and their intensity increases with increasing Mn content, in contrast to those of the icosahedral phase which decrease and finally disappear in the annealed $Al_{70}Pd_{10}Mn_{20}$ sample (x=20, (b)). It is also of interest to note that annealing at 800°C raises intensity of the peaks of the decagonal phase and lowers intensity of the peaks of the icosahedral phase, as can be clearly seen in the sample of x=15. The results were also confirmed by electron microscopic studies of these samples, and it was found that the decagonal quasicrystal grains appear with definite orientational relationships to adjacent icosahedral grains. These relationships were the same as those reported previously in the Al–Mn system.[13] These observations suggest that the decagonal quasicrystal phase coexists with the icosahedral quasicrystal phase in the composition range x=10–15 at 800°C and that a part of the major icosahedral phase in the as-cast samples transforms to the decagonal quasicrystal so as to establish an equilibrium ratio at 800°C. Most of the diffraction peaks in the pattern of the annealed $Al_{70}Pd_{10}Mn_{20}$ sample (x=20, (b)) belong to a decagonal quasicrystal phase with six layers along the ten-fold axis, and so a stoichiometric composition of the decagonal

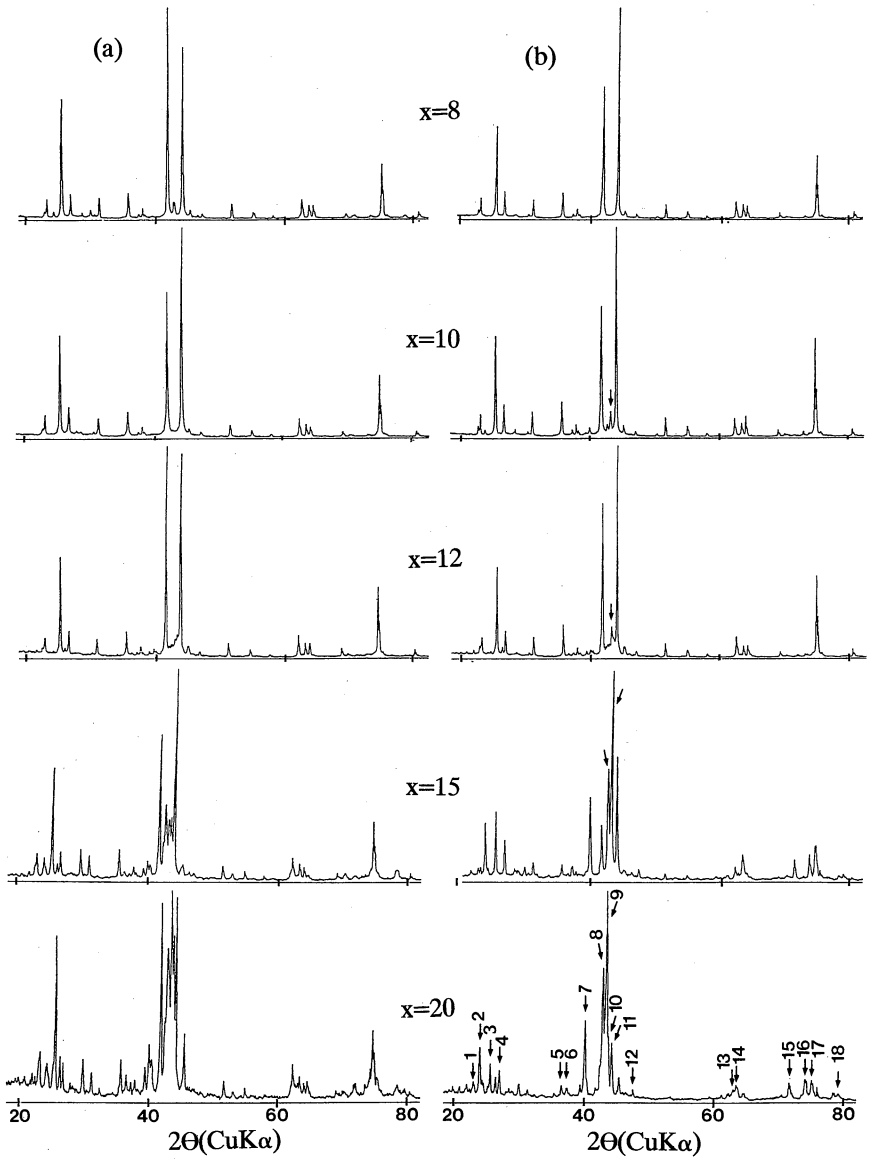

Fig. 1. X-ray diffraction patterns of $Al_{70}Pd_{30-x}Mn_x$ alloys (x=8–20) as-cast (a), and annealed at 800°C for 16 h and then quenched in water (b). The diffraction peaks indicated with the numbers in x=20 (b) are listed with indices in Table I.

phase is close to $Al_{70}Pd_{10}Mn_{20}$ and this is confirmed by Energy Dispersive X-ray analysis (EDX) mentioned below. The numbered diffraction peaks in the annealed $Al_{70}Pd_{10}Mn_{20}$ alloy (Fig. 1(b), x=20), together with their indices (Koopmans *et al.*[14]) and the observed and calculated q values, are listed in Table I. The calculated q values were estimated with the crystalline component $q_d \cos\alpha = 5.051\ nm^{-1}$ and the quasicrystalline component[14] $q_d \sin\alpha = 6.159\ nm^{-1}$, which were determined by least-square fitting.

Quantitative EDX microanalysis of adjacent decagonal and icosahedral quasicrystals gave the compositions, $Al_{69.6}Pd_{13.2}Mn_{17.2}$ and $Al_{67}Pd_{25.3}Mn_{7.7}$, respectively. The composition of the decagonal phase is consistent with the value of $Al_{70.5}Pd_{13}Mn_{16.5}$ estimated by Beeli *et al.*,[11] within experimental error. The above result shows that the decagonal and icosahedral phases are stable with these different stoichiometric compositions and coexist in equilibrium at compositions between these.

Table I. Indices, and observed and calculated q values of diffraction peaks of the decagonal quasicrystal phase.

Peak No.	Index	q_{obser} (nm^{-1})	d_{calcu} (nm^{-1})
1	2 01210	16.19	16.11
2	0 10101	16.89	16.88
3	0 01110	17.96	18.12
4	0 11011	18.97	18.94
5	0 01210	25.60	25.83
6	1 11211	26.11	26.07
7	0 11211	27.98	27.96
8	2 10101	29.75	29.94
9	0 20102	30.12	30.15
10	2 00000	30.36	30.28
11	0 12021	30.73	30.65
12	1 11211	32.91	32.97
13	0 21312	42.57	42.49
14	3 12021	43.03	43.09
15	0 31013	47.76	48.06
16	2 21312	49.13	49.16
17	0 23032	49.75	49.59
18	1 02320	52.04	52.37

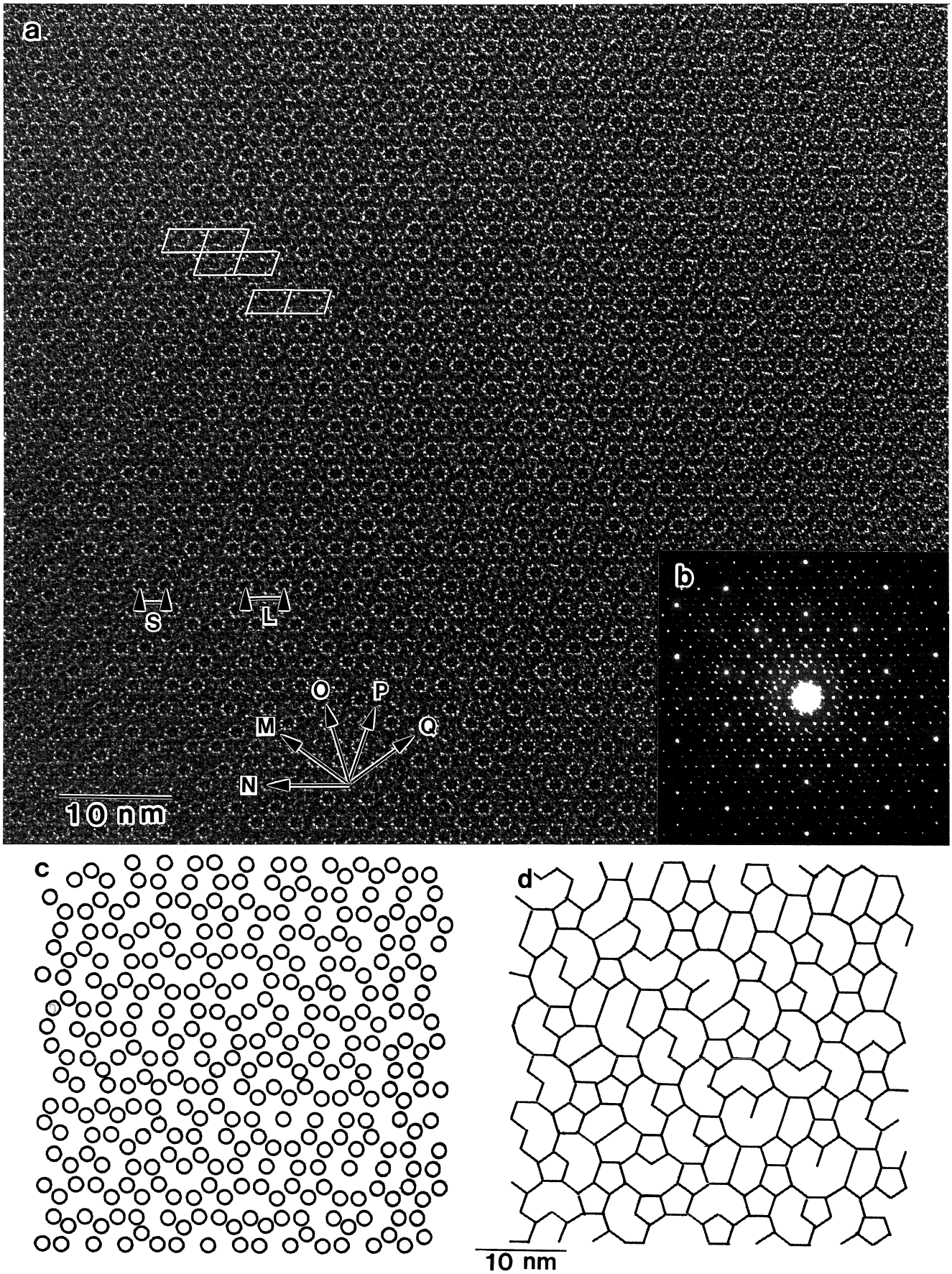

Fig 2 High-resolution micrograph (a) and electron diffraction pattern (b) of a decagonal quasicrystalline region in the $Al_{70}Pd_{13}Mn_{17}$ alloy annealed at 800°C for 4 days and then quenched in water They were taken with the incident beam parallel to the ten-fold symmetry axis In (a), some translational arrangements of parallelogram unit cells are indicated with white lines Schematical illustration (c) of the distribution of bright rings in a part of (a) and a tiling (d) constructed by connecting circles in (c) by lines

3.2 *Structure of decagonal quasicrystal*

The decagonal phase is inhomogeneous, with a distribution of various types of linear phason strain and/or microcrystalline regions in the structure. A high-resolution micrograph and an electron diffraction pattern of a relatively high-quality quasicrystalline region are shown in Figs. 2(a) and 2(b), respectively. The high-resolution image was taken from a relatively thick region to enhance the ring contrast, with the incident beam parallel to the ten-fold symmetry axis. From our recent previous observations in other alloy systems,[6-8] we have proposed that the ring contrast shows the existence of an atom cluster with decagonal symmetry. Here we will restrict ourselves to a description of the arrangement of the atom clusters, and not the atomic arrangement within the atom clusters.

The diffraction pattern of Fig. 2(b) shows a number of sharp diffraction spots, but, because of the presence of some linear phason strain, the positions of the spots are shifted from ideal positions of decagonal symmetry. The linear phason strain is observed as displacements of the arrays of bright rings in the image and the density of the displacements depends on the direction, as can be seen by obliquely viewing the observed image. Few shifts appear along the M direction, and a few shifts appear along the O and N directions, whereas a fairly high density of shifts occurs along the P and Q directions. This characteristic can be clearly seen by obliquely viewing Fig. 2(c), where the distribution of ring contrasts in a part of the observed image is schematically illustrated. From the observed image, we can see that the bright rings are distributed with two types of distances between them , S (about 2 nm) and L ($L=S\cdot\tau$, where τ is the Golden ratio). In addition, a few translational arrangements of bright rings, with a unit cell of a parallelogram with edge lengths of S and L, are observed, as indicated with white lines. A tiling, which is constructed by connecting the ring contrasts with the distances of S by lines, is shown in Fig. 2(d). Beeli *et al.*[11] proposed a different tiling from their observed high-resolution images, which is similar to the tiling of Al-Cu-Co and Al-Hi-Co decagonal quasicrystals reported previously.[6-8] Detailed examination of their images shows the tiling of Fig. 2(d) as better fit, rather than their own tiling. Our result means that structure of the decagonal quasicrystal may be interpreted by a random tiling of the decagonal atom clusters with the both S and L type linkages.

Figures 3(a) and 3(b) are a high-resolution micrograph and an electron diffraction pattern, respectively, taken with the incident beam perpendicular to the ten-fold symmetry axis, which is indicated with an arrow in Fig. 3(a). The image shows that there is a periodic arrangement of six layers, with a unit length of about 1.2 nm, along the ten-fold axis. It should be noted that there are no mistakes in the stacking sequence along the ten-fold axis.

Figure 4(a) is a high-resolution micrograph of the microcrystalline region, taken from the same ingot as that of Fig. 2(a). In the image, translational arrangements of the parallelograms with edge lengths of S and L are observed in relatively wide regions. Here, we cannot say under what conditions the decagonal quasicrystalline and crystalline structures are formed. However, it is natural for us to suggest that the structure shown in Fig. 2 shows that of the decagonal quasicrystal

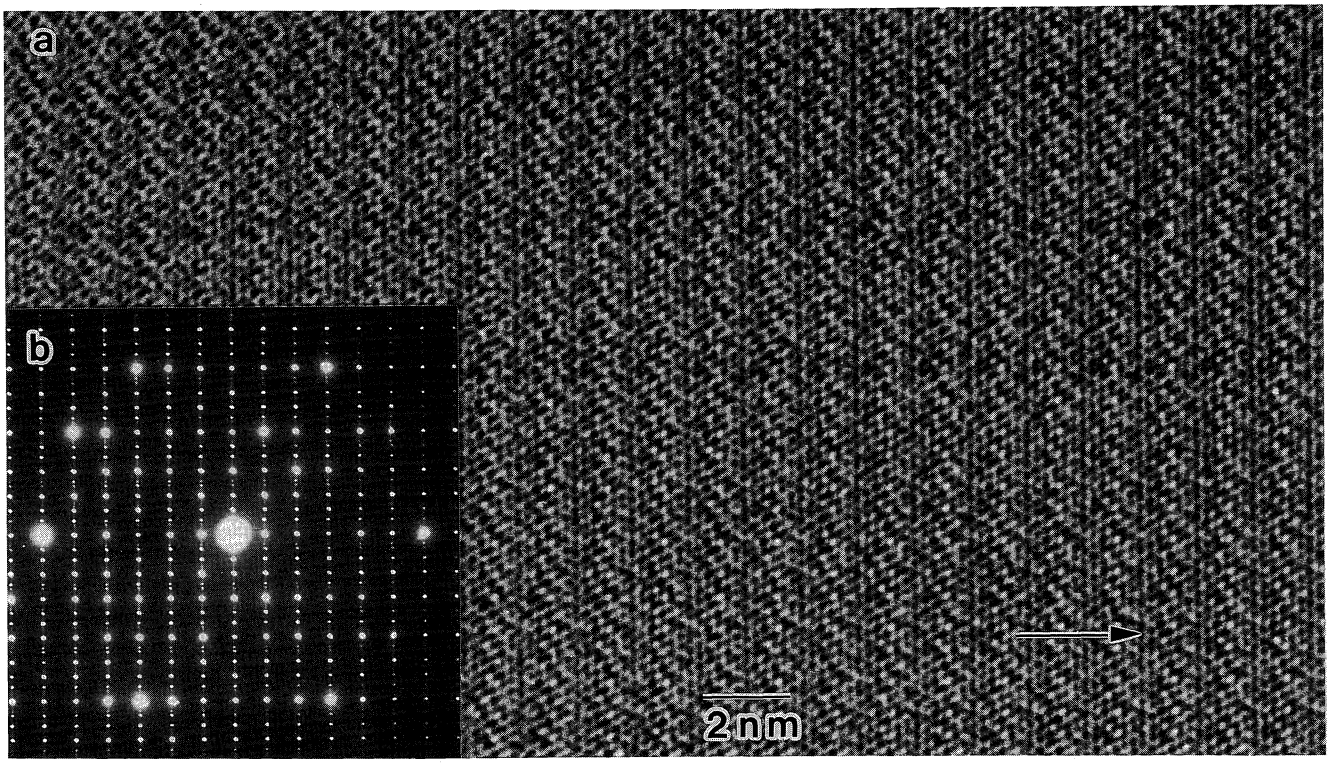

Fig. 3. High-resolution micrograph (a) and electron diffraction pattern (b) of the decagonal quasicrystal in the $Al_{70}Pd_{13}Mn_{17}$ alloy annealed at 800°C for 4 days and then quenched in water, taken with the incident beam perpendicular to the ten-fold symmetry axis.

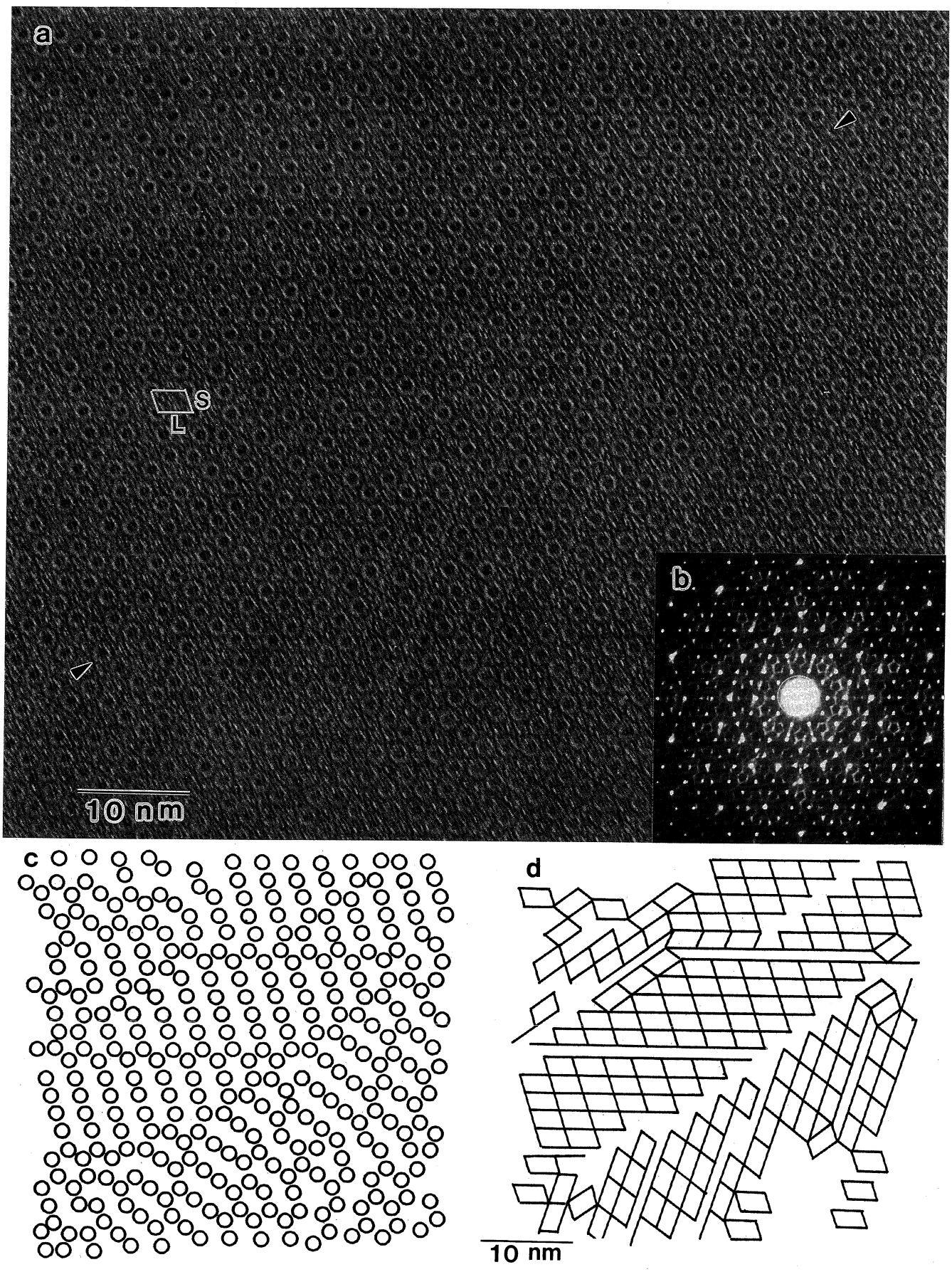

Fig. 4. High-resolution micrograph (a) and electron diffraction pattern (b) of a microcrystalline region in the $Al_{70}Pd_{13}Mn_{17}$ alloy annealed at 800°C for 4 days and then quenched in water. They were taken with the incident beam parallel to the tenfold symmetry axis. Schematical illustration (c) of the distribution of bright rings in a part of (a) and tiling (d) constructed by connecting circles in (c) by parallelogram unit cells.

of Al-Pd-Mn, though with some linear phason strain, and that of Fig. 4 is of a crystal, closely related to the decagonal quasicrystal. In the diffraction pattern of Fig. 4(b), diffuse streaks, resulting from a mixture of the microcrystalline structures, are observed. Although there are various types of boundaries between adjacent microcrystalline domains, such as antiphase boundaries, twin boundaries and so on, these boundaries are formed only with the S and L type linkages of the bright rings, as can be clearly seen in a schematical illustration of a bright ring distribution (Fig. 4(c)) and a tiling delineated with the parallelogram cells (Fig. 4(d)). This observation and the arrangement of bright rings in Fig. 2 show that the atom clusters are easily connected with the S and L type linkages with low energy in the Al-Pd-Mn decagonal phase.

By obliquely viewing Fig. 4(a) and 4(c) along the ten-fold directions, we can notice a characteristic of the bright ring rows; there are few displacements along the direction indicated with arrowheads in the image, though frequent and complex displacements along the other directions are observed. This seems to suggest that some linear phason strain produces this microcrystalline structure.

§4. Discussion and Conclusion

It is worthwhile discussing the structure of the decagonal quasicrystal of Al-Pd-Mn by comparing it with that of Al-Ni-Co and Al-Cu-Co decagonal quasicrystals. Figures 5(a) and 5(b) show tilings of a decagonal quasicrystal and microcrystalline region of Al-Cu-Co, respectively.[8] We can see that the tiling in the Al-Cu-Co decagonal quasicrystal (Fig. 5(a)) is formed mainly with two types of distances of atom clusters, SS and S, where the S is the same as the S in Fig. 2, and SS is equal to S/τ. On the other hand, in the tiling of Al-Pd-Mn in Fig. 2, the linkage SS is absent and the L linkages appear instead. These characteristics may be attributable to the linkages of atom clusters in the crystals related to the decagonal quasicrystals. The crystal of Al-Cu-Co can be considered to be formed mainly with the S linkages and the SS linkages appear at boundaries between crystalline domains, as seen in Fig. 5(b), whereas the structure of the Al-Pd-Mn crystal consists of the S and L linkages and even at the boundaries between crystalline domains the SS linkage is absent, as shown in Fig. 4. Consequently the structure of the Al-Pd-Mn decagonal quasicrystal may be interpreted as an aperiodic tiling formed with the S and L linkages of atom clusters and that of Al-Cu-Co with the SS and L linkages. Both structures enable highly ordered quasicrystals with perfect decagonal Symmetry to be produced, as have been seen in the Al-Cu-Co and Al-Ni-Co decagonal quasicrystals.[6-8]

The present observations suggest that structure of decagonal quasicrystals is formed by the aggregation of atom clusters with decagonal symmetry and that various types of decagonal quasicrystals may be constructed with different tilings formed by various types of linkages of the atom clusters. These linkages have definite bond-orientational orders limited by symmetry, but with some options of bond lengths related to τ. In addition, the difference of relative values of cohesive energies of the linkages used seems to produce variety of tilings.

From the present and other recent studies of the decagonal quasicrystals,[4-8] it may be said that random tilings constructed by limited linkages of atom clusters, without special matching rules, are real structures in highly ordered decagonal quasicrystals. However, it is questionable whether the experimentally observed random tilings are consistent with that of the random tiling model,[15] in which entropy, resulting from the randomness, stabilizes quasicrystals. Recently, Burkov[16] showed that the entropy dominates over the energy term in the decagonal quasicrystal, if the layers perpendicular to the ten-fold direction are uncorrelated. However, our observation in Fig. 3 shows the strict correlation between the layers with few stacking faults.

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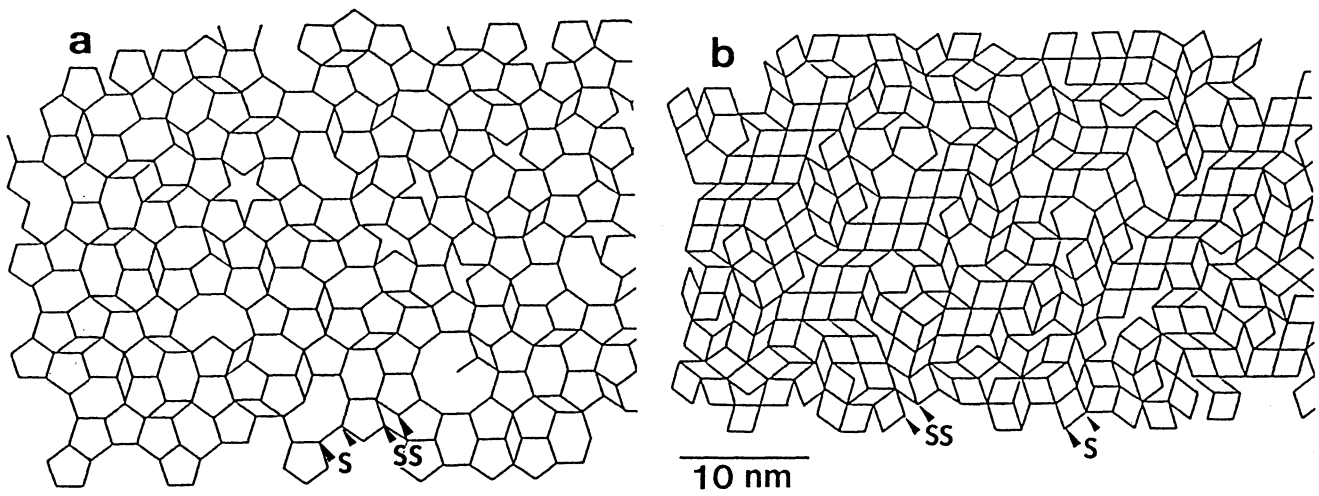

Fig. 5. Schematic illustrations of the tilings of a decagonal quasicrystal (a) and microcrystalline structure (b) in Al-Cu-Co, respectively.[8]

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References

1) A. P. Tsai, A. Inoue and T. Masumoto: Mater. Trans. JIM **30** (1989) 300.
2) A. P. Tsai, A. Inoue and T. Masumoto: Mater. Trans. JIM **30** (1989) 463.
3) L. X. He, Y. K. Wu, X. M. Meng and K. H. Kuo: Philos. Mag. Lett. **61** (1990) 15.
4) H. Chen, S. E. Burkov, Y. He, S. J. Poon and G. L. Shiflet: Phys. Rev. Lett. **65** (1990) 72.
5) P. Kaybois, M. Audier, F. Denoyer, C. Dong, J. M. Dubois and M. Lambert: Europhys. Lett. **13** (1990) 629.
6) K. Hiraga and W. Sun and F. J. Lincoln: Jpn. J. Appl. Phys. **30** (1991) L302.
7) K. Hiraga, F. J. Lincoln and W. Sun: Mater. Trans. JIM **32** (1991) 308.
8) K. Hiraga: Sci. Rep. Res. Inst. Tohoku Univ. **A36** (1991) 115.
9) A. Yamamoto, K. Kato, T. Shibuya and S. Takeuchi: Phys. Rev. Lett. **65** (1990) 1603.
10) A. R. Kortan, R. S. Becker, F. A. Thiel and H. S. Chen: Phys. Rev. Lett. **64** (1990) 200.
11) C. Beeli, H. -U. Nissen and J. Robadey: Philos. Mag. Lett. **63** (1991) 87.
12) A. P. Tsai, A. Inoue, Y. Yokoyama and T. Masumoto: Philos. Mag. Lett. **61** (1990) 9.
13) K. Hiraga, M. Hirabayashi, A. Inoue and T. Masumoto: J. Microscopy **146** (1987) 245.
14) B. Koopmans, P. J. Schurer and F. van der Woude: Phys. Rev. **B35** (1987) 3005.
15) C. L. Henley: *Quasicrystals and Incommensurate Structures in Condensed Matter*, eds. M. J. Yacaman, D. Romeu, V. Castano and A. Comes (World Scientific, Singapore, 1990) p.152.
16) S. E. Burkov: to be published in J. Stat. Phys. **65** (1991).