

New quasicrystals in $\text{Al}_{65}\text{Cu}_{20}\text{M}_{15}$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe) systems prepared by rapid solidification

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Since the discovery of an icosahedral phase with a five-fold symmetry in a rapidly solidified $\text{Al}_{86}\text{Mn}_{14}$ alloy [1, 2], the new type of structure has attracted rapidly increasing interest. Although Ti-Ni-V [3] and Pd-U-Si [4] alloys, as well as Al-based alloys, have been known as the alloy systems where the icosahedral phase is formed in a metastable state, most of the icosahedral alloys are Al-based alloys as exemplified by Al-M ($\text{M} = \text{Mn}, \text{Cr}$ or V), Al-Mg-Zn, Al-Mg-Cu, Al-Li-Cu, Al-Mn-Si, Al-Cr-Si, Al-Mn-Ge and Al-Cr-Ge etc. In addition, the present authors have recently found for the first time that the icosahedral quasicrystal is formed in Al-Cu-Fe alloys in a stable state after conventional solidification [5] as well as in a metastable state achieved by melt spinning [6]. The discovery of the stable Al-Cu-Fe quasicrystal, including a ferromagnetic iron element, is particularly notable and is expected to exert a great influence on the subsequent evolution of the study of quasicrystals. In a series of investigations, we found that the icosahedral single phase is also formed in melt-spun Al-Cu-M ($\text{M} = \text{Cr}$ or Mn) alloys and the average grain size of the quasicrystals is about $10\ \mu\text{m}$ which is 20 to 100 times as large as that of $\text{Al}_{86}\text{Mn}_{14}$ quasicrystal. This letter attempts to examine the structure, thermal stability and electrical resistivity of quasicrystalline $\text{Al}_{65}\text{Cu}_{20}\text{M}_{15}$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe) alloys and to clarify the feature of the $\text{Al}_{65}\text{Cu}_{20}\text{M}_{15}$ quasicrystals in comparison with those of the other Al-based quasicrystals reported previously.

The specimens used in the present work were $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloys. The subscripts represent nominal atomic percentages of the respective components. Mixtures of electrically pure metals were melted in an argon atmosphere using an arc furnace. Ribbon samples of about 0.02 mm thickness and 1 mm width were prepared from these mixed alloys by a single roller melt spinning apparatus. The quasicrystalline nature of the as-quenched samples was examined by X-ray diffraction, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) techniques. The methods of characterizing thermal stability and electrical resistivity have been described previously [7].

Fig. 1 shows the X-ray powder-diffraction patterns as a function of diffraction angle for rapidly solidified $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloys. Identification of the X-ray diffraction peaks corresponding to the quasicrystal with an icosahedral structure was made by using six independent Miller indices as proposed by Bancel *et al.* [8]. As indexed in Fig. 1, all the diffraction patterns consist only of quasicrystal-

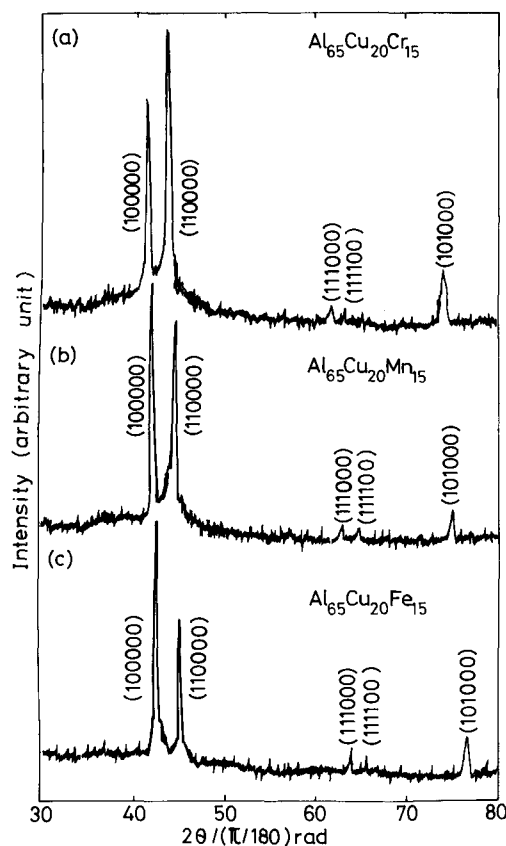


Figure 1 X-ray diffraction patterns of rapidly solidified alloys, (a) $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, (b) $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and (c) $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$.

line phase and no diffraction peaks of the other phases are seen, indicating mostly a single quasicrystalline phase with icosahedral structure is formed in the vicinity of $\text{Al}_{13}\text{Cu}_4\text{M}_3$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe) composition. No quasicrystalline single phase is formed in the other alloys of $\text{Al}_{13}\text{Cu}_4\text{M}_3$ ($\text{M} = \text{Ti}, \text{Zr}, \text{V}, \text{Nb}, \text{Co}$ or Ni). The relative intensities of each diffraction peak are different between the Al-Cu-Cr alloy and the Al-Cu-M ($\text{M} = \text{Mn}$ or Fe) alloys, suggesting the possibility that the sites of the constituent atoms are different between chromium and manganese or iron in two kinds of rhombohedrons which have been thought to be fundamental units in the icosahedral structure [9].

It has previously been shown that the quasicrystalline single phase is formed in the vicinity of 15 at % Cr and 21 at % Mn in rapidly solidified Al-Cr [10] and Al-Mn [11-13] alloys. The chromium and manganese concentrations are nearly the same level as those of the present Al-Cu-M quasicrystals. It is therefore expected that the quasicrystal is formed in the entire composition range of 0 to 20 at % Cu in $\text{Al}_{85-x}\text{Cu}_x\text{M}_{15}$ ($\text{M} = \text{Cr}$ or Mn) alloys. The rapidly solidified

TABLE I Interlattice spacing (d) and relative peak intensity (I_r) determined from the X-ray diffractometry data of icosahedral $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ quasicrystals. The data for icosahedral $\text{Al}_{84.6}\text{Cr}_{15.4}$, $\text{Al}_{77.5}\text{Mn}_{22.5}$, $\text{Al}_{60}\text{Ge}_{20}\text{Cr}_{20}$ and $\text{Al}_{60}\text{Cu}_{10}\text{Li}_{30}$ alloys taken from [10, 13–15] are also shown for reference.

Index	$\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$		$\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$		$\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$		$\text{Al}_{84.6}\text{Cr}_{15.4}$		Index		$\text{Al}_{77.5}\text{Mn}_{22.5}$		$\text{Al}_{60}\text{Ge}_{20}\text{Mn}_{20}$		$\text{Al}_{60}\text{Ge}_{20}\text{Cr}_{20}$		$\text{Al}_{60}\text{Cu}_{10}\text{Li}_{30}$		
	d (nm)	I_r (%)	d (nm)	I_r (%)	d (nm)	I_r (%)	d (nm)	I_r (%)	Index	d (nm)	I_r (%)	d (nm)	I_r (%)	d (nm)	I_r (%)	d (nm)	I_r (%)	d (nm)	I_r (%)
(100000)	0.2177	69	0.2137	100	0.2111	100	0.2199	100	(100000)	0.2164	100	0.2149	100	0.2174	85	0.2377	100	0.2377	100
(110000)	0.2070	100	0.2028	65	0.2000	67	0.2088	88	(110000)	0.2056	78	0.2043	94	0.2065	100	0.2260	79	0.2260	79
(111000)	0.1498	8	0.1472	6	0.1448	9	0.1515	12	(111000)	0.1485	11	0.1481	9	0.1502	8	0.1640	6	0.1640	6
(101000)	0.1280	21	0.1757	12	0.1239	22	0.1293	17	(101000)	0.1268	20	0.1265	14	0.1280	26	0.1400	28	0.1400	28

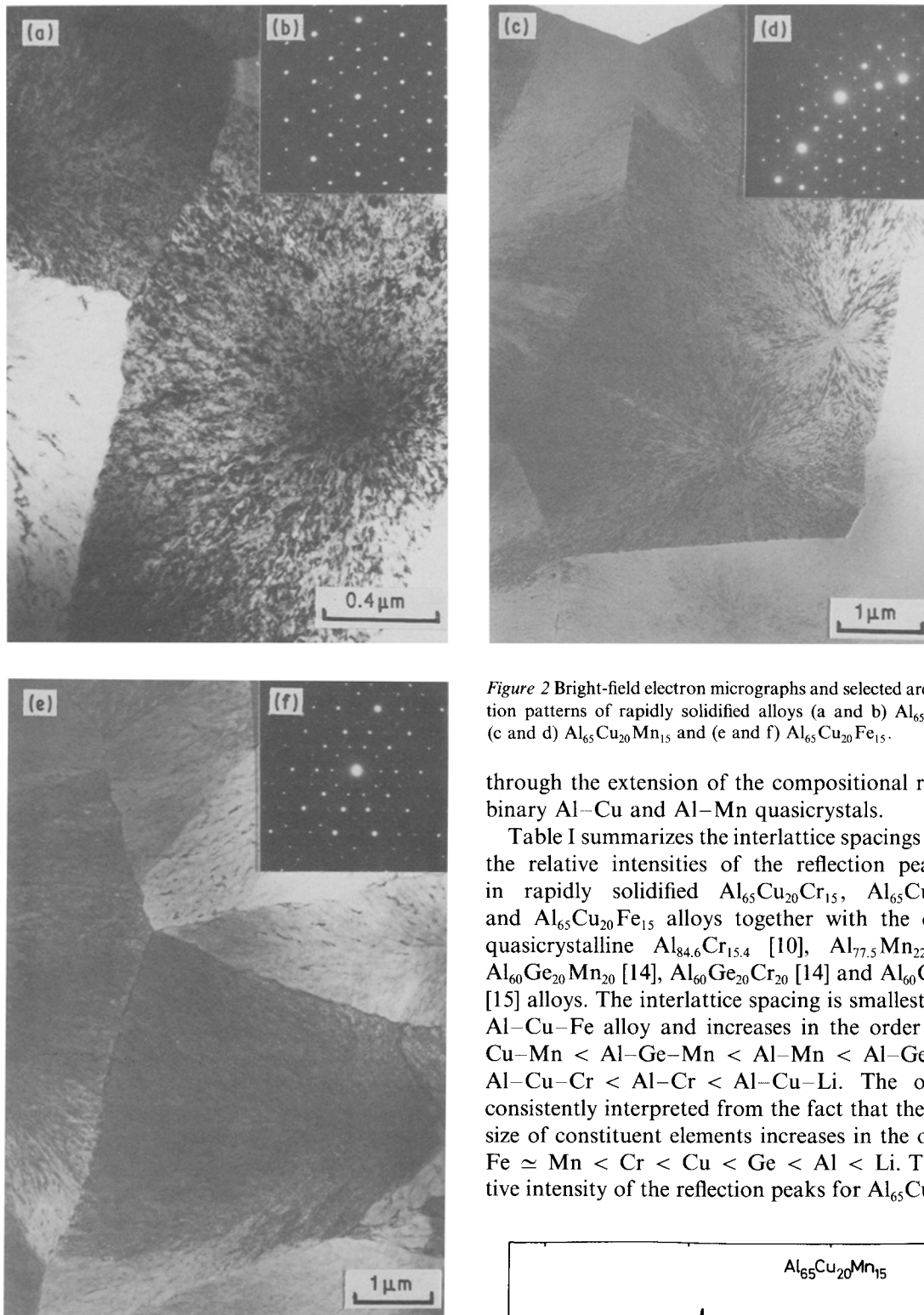


Figure 2 Bright-field electron micrographs and selected area diffraction patterns of rapidly solidified alloys (a and b) $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, (c and d) $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and (e and f) $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$.

through the extension of the compositional range of binary Al–Cu and Al–Mn quasicrystals.

Table I summarizes the interlattice spacings (d) and the relative intensities of the reflection peaks (I_r) in rapidly solidified $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloys together with the data of quasicrystalline $\text{Al}_{84.6}\text{Cr}_{15.4}$ [10], $\text{Al}_{77.5}\text{Mn}_{22.5}$ [13], $\text{Al}_{60}\text{Ge}_{20}\text{Mn}_{20}$ [14], $\text{Al}_{60}\text{Ge}_{20}\text{Cr}_{20}$ [14] and $\text{Al}_{60}\text{Cu}_{10}\text{Li}_{30}$ [15] alloys. The interlattice spacing is smallest for the Al–Cu–Fe alloy and increases in the order of Al–Cu–Mn < Al–Ge–Mn < Al–Mn < Al–Ge–Cr \approx Al–Cu–Cr < Al–Cr < Al–Cu–Li. The order is consistently interpreted from the fact that the atomic size of constituent elements increases in the order of Fe \approx Mn < Cr < Cu < Ge < Al < Li. The relative intensity of the reflection peaks for $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$

structure in $\text{Al}_{85-x}\text{Cu}_x\text{Cr}_{15}$ alloys consists of a quasicrystalline single phase at 5 at % Cu and mixed phases of quasicrystal and Al_2Cu at 10 and 15 at % Cu, and that in $\text{Al}_{85-x}\text{Cu}_x\text{Mn}_{15}$ is mixed phases of quasicrystal and Al_6Mn at 5, 10 and 15 at % Cu. Furthermore, the replacement of copper by aluminium in $\text{Al}_{65+x}\text{Cu}_{20-x}\text{Fe}_{15}$ alloys gives rise to the structural change from quasicrystal at 10 and 15 at % Fe to a mixed structure of Al + Al_3Fe + $\text{Al}_7\text{Cu}_2\text{Fe}$ at 5 at % Fe. These results allow us to conclude that the present quasicrystalline alloys belong to a new type of quasicrystal which is different from that formed

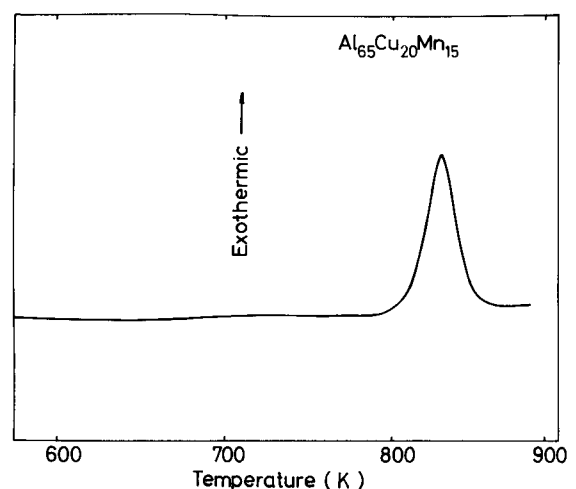


Figure 3 Differential scanning calorimetric curve of an $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ quasicrystal prepared by rapid solidification. $\Delta H_{\text{exo}} = 690 \text{ J mol}^{-1}$.

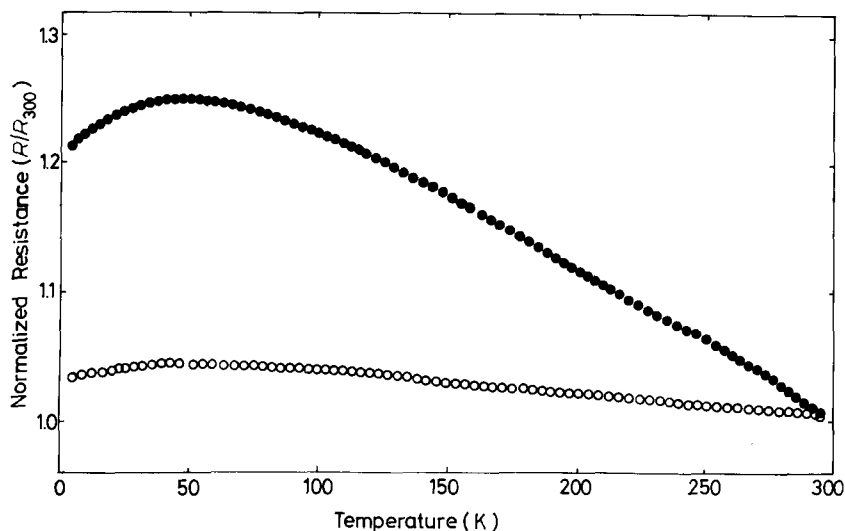


Figure 4 Change in the electrical resistivity of (○) $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, and (●) $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ quasicrystals as a function of temperature. ρ_{300} values are (○) $9.5 \mu\Omega \text{ m}$, (●) $29.5 \mu\Omega \text{ m}$.

and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ quasicrystals decreases in the order $(100000) > (110000) > (101000) > (111000)$, in agreement with the order for the other Al-based quasicrystals, while that for $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$ quasicrystal differs for the reflection peaks of (100000) and (110000) . Although the difference appears to reflect the difference of the sites where the constituent atoms occupy in the icosahedral structure, the clarification of the origin for the difference is in progress.

In order to examine whether or not a small amount of second phase precipitates along the grain boundaries of the quasicrystalline matrix, in addition to the clarification of morphology and grain size of the icosahedral quasicrystal, TEM observation was carried out for the three rapidly solidified quasicrystalline alloys. Fig. 2 shows bright-field electron micrographs and selected area diffraction patterns of $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$ (a and b), $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ (c and d) and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ (e and f). The diffraction patterns reveal a five-fold symmetry and are indexed as $[100000]_q$. As shown in the bright-field micrographs, the quasicrystals consist of large grains with an average size of about $5 \mu\text{m}$ for $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$, about $20 \mu\text{m}$ for $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and about $10 \mu\text{m}$ for $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$. Additionally, the contrast revealing radiating branches is seen in each alloy, indicating that the nucleation and growth of the icosahedral structure stem from a site near the grain boundary. Neither equiaxed subgrain boundaries nor clearly appreciable second phase are seen. It is noticeable that the grain sizes of $\text{Al}_{65}\text{Cu}_{20}\text{M}_{15}$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe) quasicrystals are 20 to 100 times as large as that (0.2 to $0.5 \mu\text{m}$) of the quasicrystals in Al–Mn [1, 2] and Al–Cr [10] systems prepared in the same melt-spinning condition and hence grain growth of the quasicrystals from liquid is thought to be much faster for the Al–Cu–M ($\text{M} = \text{Cr}, \text{Mn}$ or Fe) alloys. Considering the results that the average grain sizes of the $\text{Al}_{65}\text{Cu}_{20}\text{M}_{15}$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe) quasicrystals are as large as ~ 5 to $20 \mu\text{m}$ and no trace of second phase is seen even on the grain boundaries, the formation of the new quasicrystalline phase at compositions of $\text{Al}_{13}\text{Cu}_4\text{M}_3$ is concluded to be much easier than that for the previously reported Al-based quasicrystals, except for the Al–Cu–Li [15] system.

The transformation behaviour of the quasicrystals

to equilibrium phases was examined by DSC in a temperature range of 273 to 873 K. Fig. 3 shows the DSC curve of $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ quasicrystal measured at a heating rate of 40 K min^{-1} . The quasicrystal exhibits a large exothermic peak resulting from the transformation of quasicrystal to a crystalline structure in a temperature range of 783 to 858 K and the heat of transformation was measured as 690 J mol^{-1} . On the other hand, the Al–Cu–Cr and Al–Cu–Fe quasicrystals did not show any exothermic peak at temperatures below 873 K, indicating that the Al–Cu–Cr (or Fe) quasicrystals have a high thermal stability. The high thermal stability allows expectation of obtaining thermodynamically stable Al–Cu–Cr and Al–Cu–Fe quasicrystals and the expectation has been achieved for both quasicrystals [5, 16].

Fig. 4 shows the electrical resistivity of quasicrystals $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ as a function of temperature. The resistivity at 300 K is $9.5 \mu\Omega \text{ m}$ for the Al–Cu–Cr quasicrystal and $29.5 \mu\Omega \text{ m}$ for the Al–Cu–Fe quasicrystal, being much higher for the latter. With decreasing temperature, the resistivity increases in the range of 300 to 50 K, shows a maximum value at about 50 K and decreases in the range of 50 to 4.2 K. Thus the temperature dependence of resistivity is similar for both alloys, but the degree of the dependence is much larger for the Al–Cu–Fe quasicrystal with high electrical resistivity. The resistivity (ρ) as a function of temperature (T) varies in the approximate relation of $\rho \propto (300 - T)$ in the wide temperature range of 130 to 300 K and the temperature coefficient of resistivity (TCR) defined by $1/\rho_{273}(d\rho_{273}/dT)$ is $-2.0 \times 10^{-5} \text{ K}^{-1}$ for $\text{Al}_{65}\text{Cu}_{20}\text{Cr}_{15}$ and $-3.9 \times 10^{-5} \text{ K}^{-1}$ for $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, being about twice the size for the Al–Cu–Fe quasicrystal. The high resistivity combined with a negative temperature dependence for the Al–Cu–Cr and Al–Cu–Fe quasicrystals is different from the results for Al–Cr [10] and Al–Mn [17] quasicrystals where a slightly positive temperature dependence was observed.

In conclusion, it was found that new quasicrystals in Al–Cu–Cr, Al–Cu–Mn and Al–Cu–Fe systems are formed in the vicinity of $\text{Al}_{65}\text{Cu}_{20}\text{M}_{15}$ ($\text{M} = \text{Cr}, \text{Mn}$ or Fe). It is particularly notable that the quasicrystalline structure in the Al–Cu–Cr and Al–Cu–Fe

alloys remains stable up to a temperature greater than 873 K. This led to the formation of a thermodynamically stable quasicrystal in conventionally solidified Al-Cu-Cr [16] and Al-Cu-Fe [5] alloys.

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