

## Phase transformations and structure characteristics of the $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$ decagonal phase

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 1665

(<http://iopscience.iop.org/0953-8984/3/11/023>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 22:57

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

# Phase transformations and structure characteristics of the $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$ decagonal phase

Chuang Dong†, Jean Marie Dubois†, Marc De Boissieu‡ and Christian Janot§

† Laboratoire de Science et Génie des Matériaux Métalliques, CNRS URA 159, Ecole des Mines, Parc de Saurupt, F-54042 Nancy, France

‡ Laboratoire de Thermodynamique et Physico-Chimie Métallurgique, CNRS UA 29, ENSEEG, BP75, F-38402 Saint-Martin d'Hères, France

§ Institut Laue Langevin, BP156X, F-38042 Grenoble, France

Received 19 December 1990

**Abstract.** The phase transformations and structure characteristics of the  $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$  alloy were studied by neutron diffraction. The scheme of Yamamoto and Ishihara can satisfactorily index the diffraction patterns. The Al–Cu–Co decagonal phase is stable in the temperature range between 973 and 1350 K. At the low temperature end it relaxes to a microcrystalline approximant structure. At the high temperature end, it melts directly into liquid. The scheme of Yamamoto and Ishihara can perfectly index the neutron powder diffraction patterns ( $a = 7.212 \text{ \AA}$ ,  $c = 4.184 \text{ \AA}$  at 973 K). We propose that it is the average quasiperiodic sublattice that determines the powder diffraction characteristics of the microcrystalline structure at room temperature which can also be indexed in decagonal phase notation.

Previously, detailed structural studies of  $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$  single crystals have been performed by means of x-ray diffraction (Launois *et al* 1990) and high resolution electron microscopy (Audier *et al* 1990, Dong *et al* 1990b). The results showed that this material is not really a decagonal phase at room temperature as claimed in earlier work (He *et al* 1988, Tsai *et al* 1989). Instead, a microcrystalline structure has been revealed that, however, gives diffraction patterns which resemble quite well those of the decagonal phase. It has been pointed out that a very small number of basic structure elements (pentagon, convex pentagon and rhombus) can be used to construct the Penrose tiling or other orthorhombic approximant phases, depending on the local ordering imposed (Dong *et al* 1990b). A transition from this microcrystalline structure to the decagonal phase has also been observed during *in situ* heating in the microscope (Audier *et al* 1990). Thus, this alloy is in many ways similar to the AlCuFe alloy in which a high temperature stable icosahedral phase undergoes a reversible transition to a rhombohedral microcrystalline approximant structure upon cooling down to room temperature (Audier and Guyot 1989, Bancel 1989, Dubois *et al* 1990, Dong *et al* 1990a).

In this letter, we will present neutron diffraction studies of an  $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$  sample in which a stable decagonal phase is supposed to exist. Emphasis will be put on the phase transformations concerning the decagonal phase and on the structure characteristics of the decagonal phase. The samples for the present experiment were prepared by RF

melting of pure elemental metals. The cylinder ingots so obtained were measured by neutron diffraction performed on the D1B and D2B diffractometers at the Institut Laue Langevin in Grenoble. The D1B diffractometer was used in real-time diffraction mode thanks to its 400-cell position sensitive detector. Its angular resolution is limited to  $0.02^\circ$ . The D2B facility is a high resolution two-axis diffractometer with  $\Delta Q/Q = 5 \times 10^{-3}$  ( $Q = 4\pi \sin \theta/\lambda$ ). Thus, the former instrument was chosen to record in real time the phase transformation processes on heating and cooling the sample and the latter was used to obtain high resolution neutron diffraction diagrams at several chosen temperatures. For more experimental details, the reader is referred to Pannetier *et al* (1987), Dong *et al* (1990a) and Janot *et al* (1990).

To begin with, we show in figure 1 a high-resolution neutron diffraction diagram taken at 973 K, in order to give an overall view at the Al-Cu-Co decagonal phase (wavelength  $\lambda = 1.593 \text{ \AA}$ ). The scheme of Yamamoto and Ishihara (1988) can perfectly index the whole pattern with quasilattice parameter  $a = 7.212 \text{ \AA}$  perpendicular to the 10-fold axis and quasilattice stacking periodicity  $c = 4.184 \text{ \AA}$  along the 10-fold axis (see table 1). The good agreement between experimental and calculated values indicates that the sample does not contain crystalline phase impurities. The measurements at the other temperatures (1083 K, 873 K, 773 K and room temperature) give essentially the same diffraction patterns and all can be indexed in the decagonal phase notation in spite of the fact that at least the room temperature state corresponds to a microcrystalline approximant structure (Launois *et al* 1990, Audier *et al* 1990).

Before examining the diffraction details, we first concentrate on the phase transformations concerning the decagonal phase in order to discover exactly in which temperature range the true decagonal phase exists. Figure 2 is the 3-dimensional view of the evolution of diffraction patterns (corrected for background intensity,  $\lambda = 2.52 \text{ \AA}$ ) during a heating run from room temperature to 1333 K with a heating rate of  $4.8 \text{ K min}^{-1}$ . Two reactions are visible. The first one is signalled by a rise of diffraction intensities at about 950 K while no peak disappears or appears. Besides, the peak widths also show a significant decrease upon heating as illustrated in figure 3. Here high-resolution neutron diffraction data from the D2B diffractometer are used. Note that for  $Q = 3.14 \text{ \AA}^{-1}$ , the D2B instrument resolution is  $0.40^\circ$  in  $2\theta$  units, which is almost equal to the (15630) peak width at the highest temperature reached by the specimen. The rise of peak intensity and sharpening of peak width reflect a certain kind of ordering in the original microcrystalline approximant structure and are supposed to be due to a transition to the real decagonal phase. This point of view is supported on the one hand by *in situ* heating observation in an electron microscope (Audier *et al* 1990) and on the other by the analogy to the solid state transition from rhombohedral microcrystalline approximant structure to the high temperature stable icosahedral phase in the Al-Cu-Fe alloy (Audier and Guyot 1989, Bancel 1989, Dong *et al* 1990a, Dubois *et al* 1990). The peak intensities reach a maximum at about 1000 K. At about 1170 K, the peak intensities begin to fall rapidly; at the same time, the presence of some liquid alloy becomes visible as revealed by a rise in background intensity. This is a reaction in which the decagonal phase decomposes into liquid. As the maximum heating temperature was limited by the furnace capacity, the full liquid state has not been achieved. To compensate for this, a differential thermal analysis (DTA) experiment was performed afterwards with the same specimen. Figure 4 shows a DTA curve during a heating run with a heating rate of  $15 \text{ K min}^{-1}$ . Two peaks are present at 980 and 1355 K that correspond to the solid state transition from microcrystalline approximant structure to the decagonal phase and the complete melting of the decagonal phase, respectively. Thus, the decagonal phase is stable in the temperature

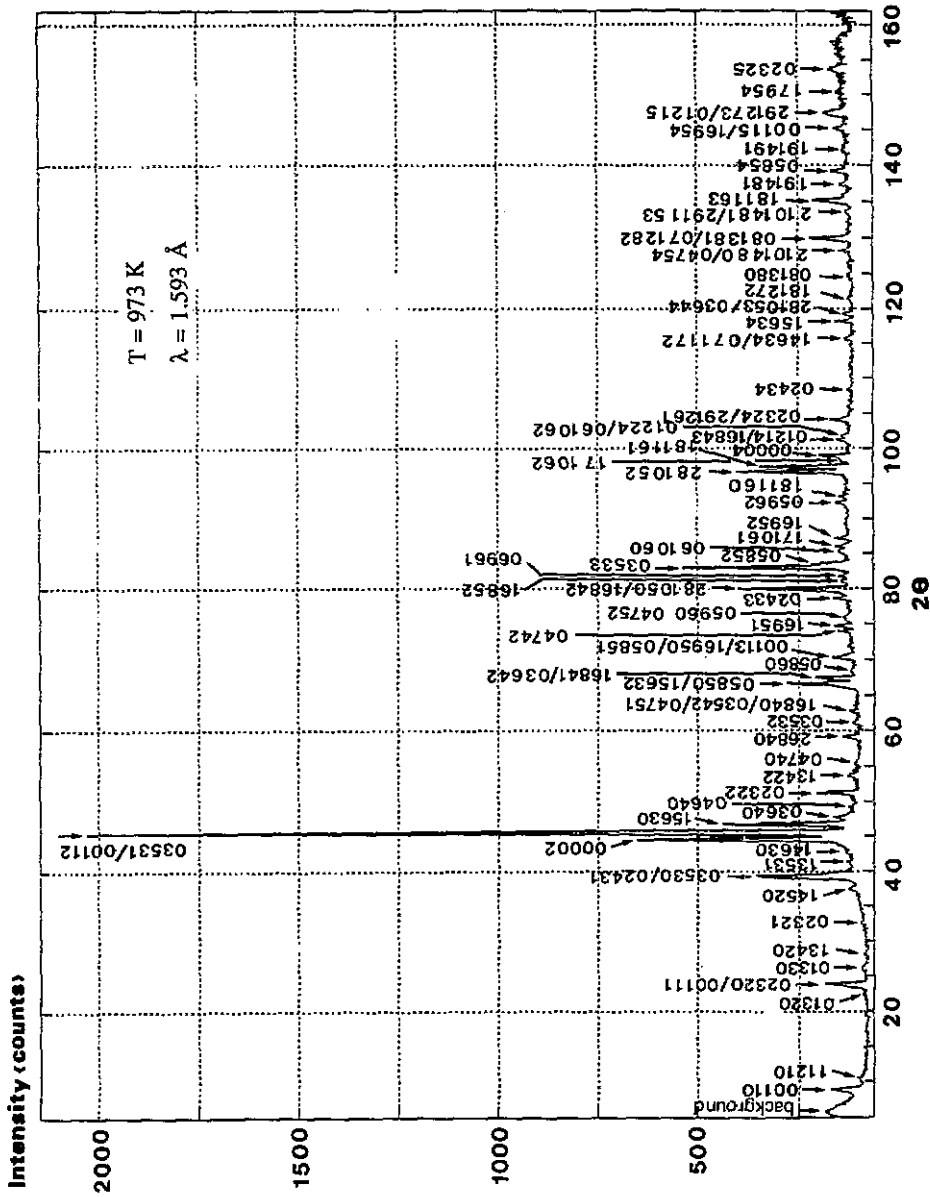


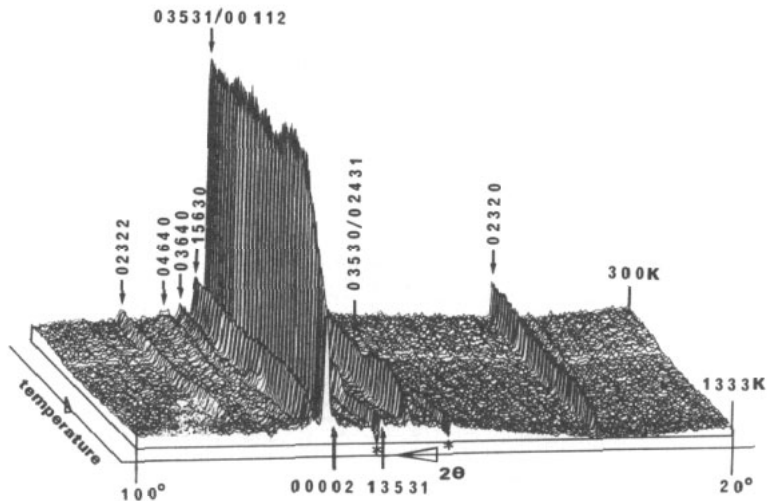
Figure 1. High-resolution neutron diffraction diagram of the  $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$  sample taken at 973 K with wavelength  $\lambda = 1.593 \text{ \AA}$ . It can be indexed according to decagonal phase notation (Yamamoto and Ishihara 1989) with  $a = 7.212 \text{ \AA}$ ,  $c = 4.184 \text{ \AA}$ . The first broad peak on the left is from background scattering.

Table 1. The indexing of the Al-Cu-Co decagonal phase at 973 K.

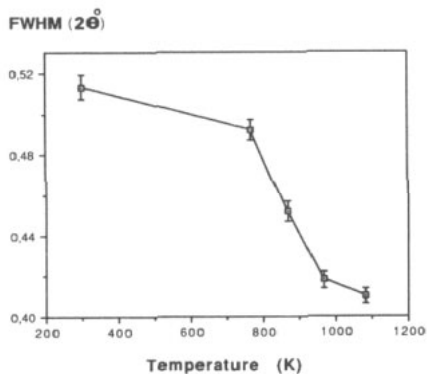
Indices					Experimental		Indices					Calculated <sup>a</sup>		Experimental		
$n_1$	$n_2$	$n_3$	$n_4$	$n_5$	$Q_1$	Int.	$n_1$	$n_2$	$n_3$	$n_4$	$n_5$	$Q_1$	$Q_{per}$	$Q_1$	$Q_{per}$	Int.
0	0	1	1	0	0.630	0.618	0	3	5	3	3	5.237	0.146	5.234	0.146	169.07
1	1	2	1	0	0.741	1.176	0	5	8	5	2	5.262	0.090	5.255	0.090	66.54
0	1	3	2	0	1.574	0.821	0	6	10	3	0	5.341	0.292	5.345	0.292	10.82
0	0	1	1	1	1.629	0.618	1	7	10	6	1	5.394	0.418	5.390	0.418	10.75
0	2	3	2	0	1.650	0.236	1	6	9	5	2	5.456	0.548	5.451	0.548	10.50
0	1	3	3	0	1.809	1.199	1	5	9	6	2	5.701	0.596	5.699	0.596	14.48
1	3	4	2	0	1.940	0.449	1	8	11	6	0	5.739	0.225	5.739	0.225	9.04
0	2	3	2	1	2.231	0.236	2	8	10	5	2	5.901	0.172	5.900	0.172	126.91
1	4	5	2	0	2.547	0.507	1	8	11	6	1	5.932	0.225	5.932	0.225	112.06
0	2	4	3	1	2.657	0.590	1	7	10	6	2	5.989	0.419	5.981	0.419	20.25
0	3	5	3	0	2.670	0.146	0	0	0	0	4	6.007	0.000	6.002	0.000	30.72
1	3	5	3	1	2.803	1.054	0	1	2	1	4	6.093	0.382	6.102	0.382	12.51
0	0	0	0	2	3.003	0.000	1	6	8	4	3	6.106	0.314	6.102	0.314	12.51
0	3	5	3	1	3.064	0.146	0	1	2	2	4	6.125	0.727	6.126	0.727	11.72
0	0	1	1	2	3.069	0.618	0	6	10	6	2	6.128	0.292	6.126	0.292	11.72
1	5	6	3	0	3.139	0.278	0	2	3	2	4	6.229	0.236	6.229	0.236	25.67
0	3	6	4	0	3.202	0.677	2	9	12	6	1	6.241	0.502	6.229	0.502	25.67
0	2	3	2	2	3.427	0.236	0	2	4	3	4	6.394	0.590	6.405	0.590	3.98
1	3	4	2	2	3.576	0.449	1	4	6	3	4	6.682	0.741	6.685	0.741	12.68
0	4	7	4	0	3.691	0.529	0	7	11	7	2	6.684	0.326	6.775	0.326	18.29
2	6	8	4	0	3.880	0.898	1	5	6	3	4	6.778	0.278	6.775	0.278	18.29
0	3	5	3	2	4.019	0.146	2	8	10	5	3	6.790	0.172	6.808	0.172	11.04
0	4	7	5	1	4.113	0.652	0	3	6	4	4	6.807	0.677	6.808	0.677	11.04
0	3	5	4	2	4.117	0.886	1	8	12	7	2	6.885	0.403	6.887	0.403	10.19
1	6	8	4	0	4.122	0.314	0	8	13	8	0	6.991	0.056	6.990	0.056	8.37

0	5	8	5	0	4.321	0.090	4.317	15.35	2	10	14	8	0	7.094	0.729	7.101	11.59
1	5	6	3	2	4.345	0.278	4.343	89.25	0	4	7	5	4	7.123	0.652		
1	6	8	4	1	4.387	0.314	4.388	54.40	0	8	13	8	1	7.151	0.056	7.151	64.81
0	3	6	4	2	4.390	0.677			0	7	12	8	2	7.153	0.603		
0	5	8	6	0	4.457	1.074	4.448	7.11	2	10	14	8	1	7.251	0.729	7.250	6.00
0	0	1	1	3	4.549	0.618	4.549	32.89	2	9	11	5	3	7.252	0.536		56.69
1	6	9	5	0	4.555	0.548			1	8	11	6	3	7.296	0.225	7.295	9.90
0	5	8	5	1	4.574	0.090			1	9	14	8	1	7.366	0.664	7.352	
0	4	7	4	2	4.758	0.528	4.758	11.62	0	5	8	5	4	7.400	0.090	7.397	24.31
1	6	9	5	1	4.797	0.548	4.796	18.16	1	9	14	9	1	7.463	0.984	7.467	12.94
0	5	9	6	0	4.845	0.596	4.841	3.80	0	0	1	1	5	7.535	0.618		
0	4	7	5	2	4.866	0.652	4.865	9.52	1	6	9	5	4	7.539	0.548	7.530	25.38
0	2	4	3	3	5.010	0.590	5.009	13.59	2	9	12	7	3	7.576	0.796		51.62
2	8	10	5	0	5.080	0.172			0	1	2	1	5	7.578	0.382	7.573	
1	6	8	4	2	5.100	0.314	5.080	132.66	0	2	3	2	5	7.688	0.236	7.682	28.67

\* Lattice parameters:  $a = 7.212 \text{ \AA}$ ,  $c = 4.184 \text{ \AA}$ .



**Figure 2.** Three-dimensional view of the evolution of diffraction patterns (corrected for background intensity, wavelength  $\lambda = 2.52 \text{ \AA}$ ) during a heating run from room temperature to 1333 K with heating rate of  $4.8 \text{ K min}^{-1}$  measured on the D1B diffractometer. \*, mark two defective cells of the detector.



**Figure 3.** Full width at half maximum (FWHM) of peak (15630) versus temperature as measured on the D2B diffractometer.  $Q = 3.14 \text{ \AA}^{-1}$ .

range between 973 and 1350 K (corrected for heating rate). Note that the second reaction starts at about 1070 K, soon after the end of the first reaction. Thus, the decagonal phase coexists with liquid over a large temperature range. This indicates that, upon cooling from the liquid, the decagonal phase grows directly from the liquid and no other crystalline phase is involved in the growth process. This is why well faceted single crystals can be easily obtained in the AlCuCo alloy, in contrast to the AlCuFe alloy in which the icosahedral phase grows in a peritectic reaction involving the monoclinic  $\text{Al}_{13}\text{Fe}_4$  phase and residual liquid (Dong *et al* 1990a, Dubois *et al* 1990).

Most of the peaks visible in figure 2 show an obvious rise at the transition from the microcrystalline approximant structure to the decagonal phase. All the corresponding planes have quasiperiodic components, i.e. the quasilattice indices  $n_1, n_2, n_3, n_4$  are not all equal to 0. But if we look at the purely periodic (00002) peak that hides behind the strong (03531, 00012) peaks in figure 2, we find a completely different behaviour:

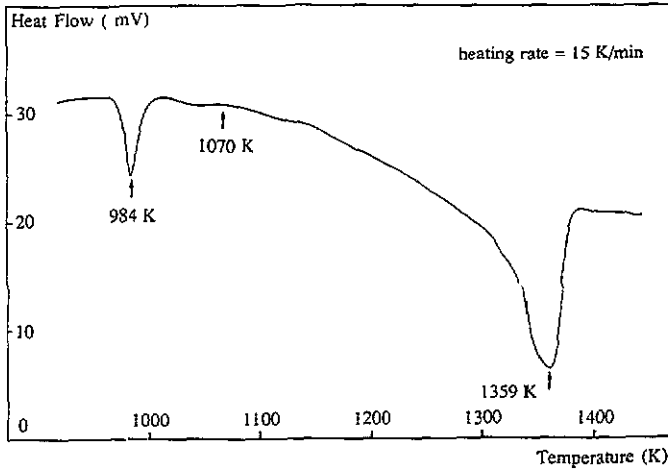


Figure 4. DTA heating curve of the  $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$  alloy with a heating rate of  $15 \text{ K min}^{-1}$ .

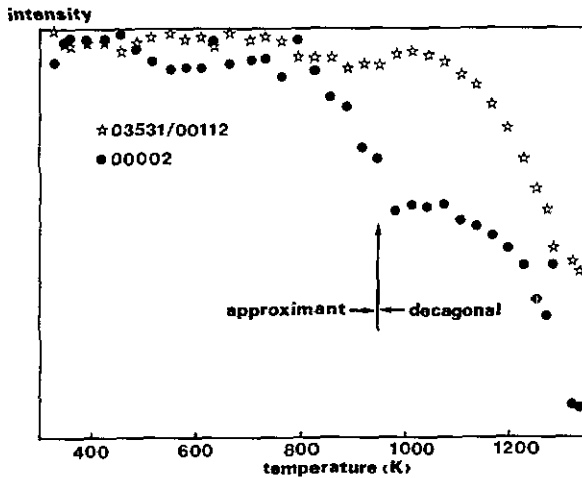


Figure 5. Integrated intensities of peaks (03531, 00012) and (00002) as a function of temperature during the heating from room temperature to 1333 K. Note that the two peak intensities are normalized in such a way that the maximum intensity is 100. The arrow marks the moment when the microcrystalline approximant structure begins to transform to the decagonal phase.

instead of rising, its intensity decreases as the solid state transition begins (figure 5). Thus, during this transition, the 2-dimensional ordering on quasiperiodic planes and the 1-dimensional periodicity perpendicular to it behave in different ways. This may be related to the different temperature dependences of quasilattice parameter  $a$  and quasilattice stacking periodicity  $c$ . An important feature of the decagonal phase is that as a 2-dimensional quasicrystal, it is not an isotropic structure. It is, therefore, not surprising to see in figure 6 that quasilattice parameter  $a$  and quasilattice stacking periodicity  $c$  manifest different temperature dependences: the former rises faster as



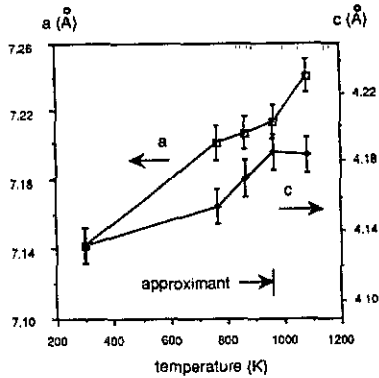


Figure 6. Different temperature dependences of quasilattice parameter  $a$  and quasilattice stacking periodicity  $c$ .

temperature goes up, indicating that the 2-dimensional quasilattice has a higher thermal expansion coefficient than the periodic direction along the ten-fold direction.

Now we turn to the analysis of some structure characteristics of this decagonal phase. Since this is only a 2-dimensional quasicrystal, we will focus on the 2-dimensional quasilattice. For the decagonal phase indexing scheme, the choice of parameter  $a$  is rather arbitrary, because an inflation or deflation by  $\tau$  ( $\tau = (1 + \sqrt{5})/2$ ) will give essentially the same result (Yamamoto and Ishihara 1989). This parameter is usually related to the 4-dimensional cubic superlattice constant. For many of the known decagonal phases (e.g. in the systems Al-Mn, Al-Fe, Al-Cu-Fe-Cr, etc), this constant is about 4.5 Å. The origin of this value has been related by Dong *et al* (1990b) to the average edge length of the smallest distorted pentagon that can be defined on the (110) atomic plane of the CsCl type of phase. This gives a physical meaning to the proper choice of the parameter  $a$ . However, in the case of the Al-Cu-Co decagonal phase, we have adopted an  $a$  parameter  $\tau$  times larger. Our choice is based on the fact that, as shown by a high-resolution electron microscopy study (Dong *et al* 1990b), the unit length of the microcrystalline approximant structure for the Al-Cu-Co(-Si) alloy is  $\tau$  times larger than that for the Al-Cu-Fe-Cr alloy, i.e. the former structure is a  $\tau$  inflation ordering based on the latter. Moreover, the peak with the smallest  $Q$  value ( $Q = 0.39 \text{ \AA}^{-1}$  at 973 K) has a simple index (00010) if  $a = 7.212 \text{ \AA}$ ; meanwhile, the index will be (01010) if  $a = 4.457 \text{ \AA}$ . This peak is observed on the x-ray single-crystal diffraction patterns (Launois *et al* 1990); but it is not observable in our neutron powder diffraction diagrams, either because it is not sensitive to neutron scattering contrast or it is just overwhelmed by the background intensity nearby (figure 1).

At the beginning of this letter, we mentioned that the powder diffraction patterns of microcrystalline approximant material can be indexed well in decagonal phase notation. However, the electron diffraction patterns cannot be totally explained by crystalline lattices plus ten-fold twinning operations (Audier *et al* 1990). The principal difference between the microcrystalline approximant structure and the decagonal phase is that the former has local periodic ordering while the latter has a quasiperiodic one. However, their long range orderings are quite similar, as their diffraction patterns are very similar. Dong *et al* (1990b) have proposed that the quasiperiodic subnetworks with basic lattice constant  $a = 4.5 \text{ \AA}$  may exist inside the unit cells of the orthorhombic approximant compounds of the decagonal phase. On the one hand, the quasiperiodic subnetwork can be periodically repeated, forming crystalline domains; on the other hand, the quasiperiodicity has the tend to expand, creating faulted structures between different

crystalline microdomains. In the microcrystalline structure, the periodic nature of crystalline domains is overwhelmed by their quasiperiodic subnetworks. The overall diffraction pattern comes from an average sublattice which is the extension of quasiperiodic subnetworks through periodic translation and ten-fold symmetry operations. This is perhaps why the powder diffraction patterns of microcrystalline approximant structure can be so well indexed according to the decagonal index notation. Compared with the real quasiperiodic lattice that can be obtained at high temperature, the room temperature approximant structure resembles a disordered quasilattice. This disordering produces Bragg peaks with increased peak width.

From the above discussions, the main conclusions can be summarized as the following.

(i) The  $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$  decagonal phase is stable in the temperature range between 973 and 1350 K. It coexists with liquid over a large temperature range above 1070 K. At the low temperature end, it transforms into a microcrystalline approximant structure. At the high temperature end, it melts directly into liquid.

(ii) The scheme of Yamamoto and Ishihara (1988) can perfectly index the neutron powder diffraction patterns with  $a = 7.212 \text{ \AA}$  and  $c = 4.184 \text{ \AA}$  at 973 K.

(iii) This decagonal phase has a non-isotropic structure. The 2-dimensional quasilattice and 1-dimensional periodicity show different behaviour during the solid phase transformation.

(iv) It is the average quasiperiodic sublattice that imposes the main diffraction features of the microcrystalline approximant structure. Thus it is justified that the powder diffraction patterns of microcrystalline approximant structure at room temperature can also be indexed in decagonal phase notation.

We gratefully acknowledge the Institut Laue Langevin for the allocation of beam time. We are greatly indebted to Dr J Pannetier for his support during the experiments.

## References

- Audier M and Guyot P 1989 *3rd Int. Workshop on Quasicrystals (Mexico, 1989)*  
Audier M, Launois P, Denoyer F, Lambert M, Dong C and Dubois J M 1990 *J. Microsc.* submitted  
Bancel P A 1989 *Phys. Rev. Lett.* **63**–25 2741  
Dong C, Dubois J M, De Boissieu M and Janot C 1990a *J. Phys.: Condens. Matter* **2** 6339  
Dong C, Dubois J M, Kang S S and Audier M 1990b *Phil. Mag.* submitted  
Dubois J M, Janot C, Dong C, De Boissieu M and Audier M 1990 *Troisième Coll. D'Expression Française sur les Transitions de Phases (Djerba, Tunisia)*, *Phase Trans.* submitted  
He L X, Zhang Z, Wu Y K and Kuo K H 1988 *EUREM 88 (Int. Phys. Conf. Ser. 92–3)* (Bristol: Institute of Physics) 501  
Janot C, Audier M, De Boissieu M and Dubois J M 1990 *Europhys. Lett* submitted  
Launois P, Audier M, Denoyer F, Dong C, Dubois J M and Lambert M 1990 *Europhys. Lett.* at press  
Pannetier J, Dubois J M, Janot C and Bilde A 1987 *Phil. Mag. B* **55** 435  
Tsai A P, Inoue A and Masumoto T 1989 *Mater. Trans.* **30** 42  
Yamamoto A and Ishihara K N 1988 *Acta. Crystallogr. A* **44** 707