Chemical trends of icosahedral order in Al–Cu–TM quasicrystals

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Received 20 May 1994; in final form 9 October 1994

Abstract

Icosahedral alloys with the composition Al_{62}Cu_{25.5}TM_{12.5} (TM = V, Cr, Mn, Fe, Co, Ni) were prepared by melt spinning. Prevailing icosahedral phases were found for TM = Cr, Mn and Fe. Phonon and random phason disorder were evaluated by an analysis of X-ray diffraction linewidths. A marked chemical trend was noted for phonon-type disorder, which increases in the sequence Fe < Mn < Cr. The parameter of the hypercubic lattice for the Mn-based icosahedral phase allows information to be derived on the metallic valence of Mn and its local coordination via the effective atomic radius.

Keywords: Quasicrystals; Thermodynamical stability; Melt spinning

1. Introduction

The thermodynamic stability of Al–Cu–TM quasicrystals (TM, transition metal) is a topic of active investigation. The compositional fields of the equilibrium icosahedral (i) and decagonal (D) phases are restricted and occupy different positions in the composition triangle at different temperatures, but cluster in the region of Al_{63}Cu_{20}TM_{17} and Al_{63}Cu_{15}TM_{20} respectively [1]. The i and D stability regions are often surrounded by compositional fields where crystalline approximants only are stable. In these approximants, with very large unit cells, the irrational \( \tau = (1 + \sqrt{5})/2 \) number, characteristic of quasicrystals, is replaced by rational approximate values, which allow three-dimensional (3D) periodicity.

The compositional zones in which single-phase Al–Cu–TM quasicrystals are stable at different temperatures are still unknown for most systems. In as-cast Al–Cu–Co alloys, the stability fields of the D phase and D approximants within the composition triangle were established in Ref. [2]. Also, the variation of the D stability zone between 500 and 1000 °C was investigated [3].

As shown by Bessière et al. [4], i Al–Cu–Fe phases which are truly thermodynamically stable from room temperature to the melting point require a carefully balanced composition of Al_{62}Cu_{25.5}Fe_{12.5}. Compositional deviations as small as 1% cause transitions to distorted i states below 650 °C. Samples annealed at 800 °C show the i structure in a slightly broader field, including Al_{63}Cu_{24.5}Fe_{12.5}. However, they transform reversibly below 750–550 °C into a rhombohedral approximant. Quenched i Al–Cu–Fe phases around composition Al_{63.5}Cu_{24}Fe_{12.5} were found [5] to be metastable up to 400 °C and to crystallize into the rhombohedral approximant above 600 °C. The transition from quasicrystal to crystalline approximant was shown to occur in the i Al–Cu–Fe phase via transient modulated states [5,6], possibly involving mass transport [6]. The detailed stages of the quasicrystal-to-approximant transition can be formally explained by increasing linear phason strains, as shown in Ref. [7] for the D Al–Cu–Co phase.

Al–Cu–Fe i phases quenched from the melt cover a considerably larger compositional range. As reported in Ref. [8], the i phase can be obtained by melt spinning as a major phase between Al_{60}Cu_{27}Fe_{13} and Al_{67}Cu_{16}Fe_{13}, the D phase being favoured at higher Al contents.

Little is known about i Al–Cu–Mn and Al–Cu–Cr phases in melt-spun alloys [8].

These circumstances prompted us to investigate a series of Al_{62}Cu_{25.5}TM_{12.5} (TM = Cr, Mn, Fe) as-quenched i phases from the point of view of their detailed structure (phonon and random phason disorder, symmetry and parameter of the quasicubic 6D lattice) and thermodynamic stability. The as-quenched i Al–Cu–Fe phases have a measurably higher degree of disorder than those annealed at 800 °C [4]. In the latter samples, the broadening caused by disorder is very small and the diffraction lines are reduced to the instrumental width [4]. As-quenched Al_{62}Cu_{25.5}TM_{12.5} alloys (TM = V, Co, Ni), which are outside the i stability.
field [1], were also investigated with regard to their phase composition.

Previous results on metastable, as-quenched Al–TM i phases (TM = Mn, Cr, Fe, Mn–Fe, Cr–Fe, Mn–Cr) [9] suggested a correlation between increasing phonon and phason disorder and a decrease in thermal stability (as expressed by the crystallization temperature), both dependent on the nature of the TM. Lower disorder and increased thermal stability were found for TM = Mn, Cr. These elements offer a high energetic stabilization of the Al12TM local icosahedra via electronic factors.

The calculated electronic stabilization changes continuously for TMs in the 3d and 4d periods [10], showing a maximum for 3d Cr and Mn, a prediction fully confirmed by the experimental data in Ref. [9]. Thus the evaluation of the phonon and phason disorder in i phases could lead to information about the energetics of local i configurations.

2. Experimental details

Melt-quenched ribbons in the Al–Cu–TM systems (TM = V, Cr, Mn, Fe, Co and Ni) were prepared starting from the elements (purity, 99.99%). Pieces of the primary cast alloys were induction melted in a quartz crucible in an Ar atmosphere. The melt was pushed by an Ar overpressure against a copper wheel (diameter, 400 mm) revolving at 1600–1700 rev min\(^{-1}\). The resulting ribbons were 1–2 mm wide and 30–50 \(\mu\)m thick. The nominal alloy compositions Al\(_{62.5}\)Cu\(_{25.5}\)TM\(_{12.5}\) correspond to the optimal concentration reported for the Fe system [4]. Al\(_{62.5}\)Cu\(_{25.5}\)Fe\(_{12.2}\), samples with several Fe concentrations (\(x = 60–62.5\) at.%; \(y = 12.2–14.5\) at.%) (Table 1) were also prepared.

Structural investigations were performed by X-ray diffractometry (XRD) using Cu Ka radiation, monochromatized by a flat graphite crystal placed before the scintillation detector. The ribbons were glued on glass slides, forming a uniform layer. In some cases, the two sides of the ribbon (cooled in contact with the wheel and in free atmosphere respectively) were investigated separately. Flow chart records were used to determine the phase compositions of the ribbons. For linewidth measurements, the profiles of the main i lines were recorded in a step scanning regime (\(\Delta(2\theta) = 0.01^\circ\)). Full widths at half-maximum (FWHM) and integral widths were derived and used to assess the degree of phason and phonon disorder in the i phase. The resolution was \(SG_i = 4.4 \times 10^{-4} \, \text{Å}^{-1}\) (\(G_i = 2 \sin(\theta/\lambda)\)). The parameter of the hypercubic 6D lattice was determined from the peak positions of the i lines, located by a parabolic fit in the maximum range. Corrected parameters resulted from an extrapolation vs. \(\cos^2\theta\) or \(\cos \theta \cot \theta\) of the values yielded by the individual lines, thereby eliminating the instrumental aberrations. An average was taken over the Z values resulting from the two extrapolation functions.

3. Phase composition

The as-quenched ribbons with TM = Cr, Mn, Fe consist of a dominant i phase, whose degree of structural order was found to be strongly dependent on the nature of the TM. A minor crystalline phase is also present, increasing quantitatively in the sequence Cr < Mn < Fe. No segregated Al was observed, as can be seen from the fragments of the diffraction patterns displayed in Figs. 1(a)–1(c).

3.1. As-quenched Al–Cu–Fe samples

XRD showed that a dominant i phase was formed in the bulk of the ribbons. In addition, a cubic crystalline phase was observed in the as-quenched Al–Cu–Fe samples. The occurrence of this phase in the as-quenched Al–Cu–Fe samples was also reported in Refs. [4,8]. Bessière et al. [4] identified it as the FeAl simple cubic \(\beta_2\) phase with \(z = 2.92\) Å, stable above 870 °C and partly retained in the quenching process. The lattice constant of this phase was found to be slightly increased.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal composition</th>
<th>(R)</th>
<th>(v) (rev min(^{-1}))</th>
<th>Ribbon side *</th>
<th>(i(7,11)/i(8,12)) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al(<em>{62.5})Cu(</em>{25.5})Fe(_{12.2})</td>
<td>0.59 ± 0.01</td>
<td>1600</td>
<td>w</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>Al(<em>{62.5})Cu(</em>{25.5})Fe(_{12.2})</td>
<td>0.68</td>
<td>1600</td>
<td>o</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>Al(<em>{62.5})Cu(</em>{25.5})Fe(_{12.2})</td>
<td>0.49</td>
<td>1700</td>
<td>w</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>Al(<em>{62.5})Cu(</em>{25.5})Fe(_{12.2})</td>
<td>0.55</td>
<td>1700</td>
<td>o</td>
<td>1.12</td>
</tr>
<tr>
<td>5</td>
<td>Al(<em>{61.5})Cu(</em>{25.5})Fe(_{12.6})</td>
<td>2.08</td>
<td>1700</td>
<td>w</td>
<td>1.55</td>
</tr>
<tr>
<td>6</td>
<td>Al(<em>{61.5})Cu(</em>{25.5})Fe(_{12.6})</td>
<td>1.84</td>
<td>1700</td>
<td>o</td>
<td>1.01</td>
</tr>
<tr>
<td>7</td>
<td>Al(<em>{61.5})Cu(</em>{25.5})Fe(_{14.5})</td>
<td>3.91</td>
<td>1700</td>
<td>o</td>
<td>1.45</td>
</tr>
</tbody>
</table>

* Ribbon side cooled in contact with the wheel (w) or outwards (o).

b Ratio of superstructure/main line, indicative of F-type ordering.

Table 1
Composition and phases in as-quenched Al–Cu–Fe samples. \(R = \beta(211)/i(52,84)\) (ratio of peak intensities), \(v = \) speed of cooling wheel
in our samples ($a = 2.937 \pm 1 \times 10^{-3}$ Å), which could be related to the presence of Cu.

Scanning electron microscopy (SEM) investigations showed that the i Al–Cu–Fe phase consisted of densely packed grains with a characteristic radial rosette-like morphology. Their approximate composition was found by energy dispersive analysis (EDAX) to be Al$_{67.2}$Cu$_{20.4}$Fe$_{12.4}$. Thus the i phase contains slightly more Al and less Cu than the average composition, an effect also noted in Ref. [8] for as-quenched i Al–Cu–Fe. The minor cubic crystalline phase consists of branches lying in the plane of the ribbon or normal to it. Its average composition was found to be Al$_{58}$Cu$_{27}$Fe$_{15}$, in good agreement with the ordered simple
The extreme sensitivity of the thermodynamic stability to composition is illustrated by sample 7 (Table 1), with the highest Fe concentration. Annealing for 7 h at 600 °C induces almost complete crystallization into the β phase. This suggests that the ideal composition of the i Al–Cu–Fe phase, ensuring optimal stability at \( T \geq 600 ^\circ C \), lies at Fe contents slightly less than 12.2 at.% in the global alloy composition.

The primary as-cast \( A_{62.3}Cu_{25.5}Fe_{12.2} \) alloy used in ribbon preparation contains the i phase, the cubic β phase and a third phase, characterized by the above-mentioned triplet.

### 3.3. As-quenched \( A_{62}Cu_{25.5}TM_{12.5} \) (\( TM = Mn, Cr, V, Co, Ni \)) alloys

In the Al–Cu–Mn as-quenched ribbons, small amounts of distorted β-type cubic phase appear, in addition to the prevailing i phase. The only three unambiguously assigned diffraction lines \( d=2.07 \) Å (strong), \( d=2.92 \) Å and \( d=1.201 \) Å (broad and weak) fit either \( A_{62}Cu_{25}Mn_{10} \) (CsCl-type, \( a=2.979 \) Å) or its ordered variant \( A_{62}Cu_{20}Mn_{25} \) (BiF-type, \( a=5.957 \) Å). For the former indexing, the lattice constant is \( a=2.969 \pm 1 \times 10^{-3} \) Å. A broad peak with \( d \approx 2.2 \) Å suggests the presence of small amounts of D Al–Mn phase (Fig. 1(b)). The concentration of the β crystalline phase is much lower in this system than that found in the Al–Cu–Fe as-quenched samples.

The Al–Cu–Cr as-prepared ribbons show only traces of an apparently related cubic β lattice. The only line which can be unambiguously assigned to this phase yields a lattice parameter \( a=2.99 \) Å in CsCl-type indexing. This phase could not be satisfactorily attributed to any other Al–Cu–Cr compound.

For TM = V, Co and Ni, the i phase either appears in small amounts (with V) or is absent (with Co and Ni).

The \( A_{62}Cu_{25.5}V_{12.5} \) as-quenched ribbons show a mixture of crystalline \( Al_4Cu_9 \) (with a cubic lattice) and i Al–Cu–V. An amorphous fraction is also present, yielding a broad maximum around \( d=2.1 \) Å. After Inoue et al. [1], the optimal composition for the formation of the V-based i phase is \( A_{62}Cu_{12}V_{10} \). This could explain the segregation of the Cu-rich phase \( Al_4Cu_9 \) in our sample.

The \( A_{62}Cu_{25.5}Co_{12.5} \) ribbons in their as-quenched state consist of a well-structured D phase. The positions of the diffraction lines agree well with those reported by Daulton and Kelton [11]. Amounts of a crystalline cubic Al(Cu, Co) phase are also present, presumably with some additional Cu content. This result is in agreement with the equilibrium phase diagram of the Al–Cu–Co system above the partial melting point [3]. The phase diagram shows that at 1000 °C the nominal composition of our samples corresponds to an equi-

### 3.2. Annealed Al–Cu–Fe samples

Annealing above 600 °C caused the high-temperature crystalline phase to dissolve partly into the i matrix. After 7 h at 600 °C, the ratio \( R \) was reduced to 0.33 in samples 1 and 2. However, annealing the same samples for 2 h at 600 °C plus 2 h at 800 °C resulted in an increase in the β phase (\( R=0.57 \)), restoring the level of the values found for non-annealed ribbons. These observations support the high-temperature character of the crystalline β phase. Direct annealing of samples 1 and 2 for 2 h at 800 °C also induces additional very weak lines with \( d=2.21, 2.29, 2.33, 2.88 \) and 3.51 Å, suggesting an incipient decomposition process. The first three lines are also present, although very weak, in the as-cast primary alloys.

We can conclude that the Al–Cu–Fe i phase corresponding to the nominal composition \( A_{62.3}Cu_{25.5}Fe_{12.2} \) of the alloy is stable from room temperature up to 500–600 °C, but crystallization processes (mainly into the β phase) start above this temperature, being very active at 800 °C.

The concentration ratio between crystalline β and i Al–Cu–Fe is estimated in Table 1, on an arbitrary scale, by the height ratio \( R \) of the β(211) and i(52,84) diffraction lines. Cahn indices were used to denote the i Al–Cu–Fe as-quenched samples.

The primary as-cast \( A_{62.3}Cu_{25.5}Fe_{12.2} \) alloy used in ribbon preparation contains the i phase, the cubic β phase and a third phase, characterized by the above-mentioned triplet.

### 3.3. As-quenched \( A_{62}Cu_{25.5}TM_{12.5} \) (\( TM = Mn, Cr, V, Co, Ni \)) alloys

In the Al–Cu–Mn as-quenched ribbons, small amounts of distorted β-type cubic phase appear, in addition to the prevailing i phase. The only three unambiguously assigned diffraction lines \( d=2.07 \) Å (strong), \( d=2.92 \) Å and \( d=1.201 \) Å (broad and weak) fit either \( A_{62}Cu_{25}Mn_{10} \) (CsCl-type, \( a=2.979 \) Å) or its ordered variant \( A_{62}Cu_{20}Mn_{25} \) (BiF-type, \( a=5.957 \) Å). For the former indexing, the lattice constant is \( a=2.969 \pm 1 \times 10^{-3} \) Å. A broad peak with \( d \approx 2.2 \) Å suggests the presence of small amounts of D Al–Mn phase (Fig. 1(b)). The concentration of the β crystalline phase is much lower in this system than that found in the Al–Cu–Fe as-quenched samples.

The Al–Cu–Cr as-prepared ribbons show only traces of an apparently related cubic β lattice. The only line which can be unambiguously assigned to this phase yields a lattice parameter \( a=2.99 \) Å in CsCl-type indexing. This phase could not be satisfactorily attributed to any other Al–Cu–Cr compound.

For TM = V, Co and Ni, the i phase either appears in small amounts (with V) or is absent (with Co and Ni).

The \( A_{62}Cu_{25.5}V_{12.5} \) as-quenched ribbons show a mixture of crystalline \( Al_4Cu_9 \) (with a cubic lattice) and i Al–Cu–V. An amorphous fraction is also present, yielding a broad maximum around \( d=2.1 \) Å. After Inoue et al. [1], the optimal composition for the formation of the V-based i phase is \( A_{62}Cu_{12}V_{10} \). This could explain the segregation of the Cu-rich phase \( Al_4Cu_9 \) in our sample.

The \( A_{62}Cu_{25.5}Co_{12.5} \) ribbons in their as-quenched state consist of a well-structured D phase. The positions of the diffraction lines agree well with those reported by Daulton and Kelton [11]. Amounts of a crystalline cubic Al(Cu, Co) phase are also present, presumably with some additional Cu content. This result is in agreement with the equilibrium phase diagram of the Al–Cu–Co system above the partial melting point [3]. The phase diagram shows that at 1000 °C the nominal composition of our samples corresponds to an equi-
librium mixture of D phase, cubic Al(Cu, Co) and a liquid phase.

XRD can hardly distinguish between true D phases and D approximants. However, as shown by Daulton et al. [2], true D phases are stable around the composition Al_{65}Cu_{20}Co_{15}, whereas only D approximants form around Al_{65}Cu_{12}Co_{20}. We believe that our sample contains a real D phase, because its composition is closer to the former zone.

In the Ni system, the as-quenched Al_{62}Cu_{25.5}Ni_{12.5} ribbons contain a mixture of crystalline phases, with a prevailing Al_{2}Cu_{2}Ni (CsCl-type) phase.

Due to the low content (or absence) of the i component, only the phase composition was investigated for the V-, Co- and Ni-based alloys.

4. Phonon and phason disorder in as-quenched Al–Cu–TM i phases

The presence of a dominant i phase in the as-quenched samples with TM = Fe, Mn and Cr, showing characteristic well-separated diffraction peaks, allows line-widths to be used to assess the degree of phonon and phason disorder.

The deviation from perfect i order was characterized using the relation [12]

\[ B^2 = AG^2 + CG^2 + D \]

Eq. (1) provides the most general description of disorder in the case of mixed phonon and random phason strain [9]. The parameters A and C measure the phonon and random phason disorder respectively, while D takes into account the limited coherence length ("size effect"). The effect of dislocations in quasicrystals is also described by a law of this type [12].

Figs. 2(a)–2(c) display the dependence of the line-widths on the reciprocal vector \( G \) for the as-quenched Al–Cu–Fe, Al–Cu–Mn and Al–Cu–Cr i phases. A rather complex dependence on \( G \) is observed for all samples, indicative of mixed phonon and phason disorder [9].

The parameters A and C were derived by a best fit of the experimental data to Eq. (1), using both measures of linewidth: FWHM and integral. The least-squares fit was performed in two ways.

1. Linewidths were weighted by the square of the integrated intensity in order to diminish the influence of very weak lines (whose linewidth cannot be reliably measured). The numbers of i diffraction lines used in the fit were 13 (for Al–Cu–Fe), 9 (for Al–Cu–Mn) and 7 (for Al–Cu–Cr).

2. A small number of lines, with strongly deviating widths, were eliminated from the fit, thereby significantly reducing the value of the residual. These lines were: (14,21) for Al–Cu–Fe; (7,11), (8,12) and (6,9) for Al–Cu–Mn; (11,16) and (40,64) for Al–Cu–Cr.

Al–Cu–Cr. The increased errors in the linewidth estimation could be attributed in each case to the partial superpositions of the weak i lines on those contributed by the minor crystalline phase.

Table 2 shows the A and C values derived for as-quenched i phases in the three systems. Also shown are the values obtained for metastable, as-quenched Al–Mn and Al–Cr phases [9], prepared in the same conditions. The reciprocal vectors \( G \) for each diffraction line are defined as.

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**Fig. 2.** FWHM vs. reciprocal vector \( G \) for Al–Cu–TM i phases:

(a) Al_{62.3}Cu_{25.3}Fe_{12.2}; (b) Al_{62}Cu_{25.3}Mn_{12.5}; (c) Al_{62}Cu_{25.3}Cr_{12.5}.
Table 2
Structural parameters for Al–Cu–TM i phases as derived from FWHM or integral linewidths $\beta$, $A$, phonon-type disorder parameter; $C$, phason-type disorder parameter; REZ, residual of the fit to Eq. (1); $Z$, quasicubic lattice parameter; $R_{TM}$, metallic radius (for 12 ligands); $e/a$, Hume–Rothery factor; $\lambda$, size factor

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>$A \times 10^2$ FWHM $\beta$</th>
<th>$C \times 10^2$ FWHM $\beta$</th>
<th>REZ $\times 10^3$</th>
<th>$Z$ (Å)</th>
<th>$R_{TM}$ (Å)</th>
<th>$e/a$</th>
<th>$\lambda$</th>
<th>$i(7,11)/i(8,12)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_{122}Cu_{26}Fe_{12}$</td>
<td>0.29 ± 0.08 *</td>
<td>0.07 ± 0.03</td>
<td>0.37 ± 0.15</td>
<td>0.41 ± 0.13</td>
<td>4.5</td>
<td>6.335 ± 1 × 10$^{-3}$</td>
<td>1.260</td>
<td>1.80</td>
</tr>
<tr>
<td>$Al_{122}Cu_{26}Mn_{12}$</td>
<td>0.84 ± 0.02</td>
<td>1.04 ± 0.13</td>
<td>0.43 ± 0.05</td>
<td>0.60 ± 0.10</td>
<td>1.1</td>
<td>6.415 ± 1 × 10$^{-3}$</td>
<td>1.268</td>
<td>1.68</td>
</tr>
<tr>
<td>$Al_{122}Cu_{26}Cr_{12}$</td>
<td>1.52</td>
<td>2.51</td>
<td>0.56</td>
<td>1.06</td>
<td>0.4</td>
<td>6.480 ± 1 × 10$^{-3}$</td>
<td>1.276</td>
<td>1.56</td>
</tr>
<tr>
<td>$Al_{12}Mn_{14}$</td>
<td>0.88–2.66 $^d$</td>
<td>–</td>
<td>0.50–0.86</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$Al_{12}Cr_{14}$</td>
<td>1.69 $^f$</td>
<td>–</td>
<td>0.67</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Average value and difference between values obtained with: (1) weighting by squared integrated intensities and (2) elimination of 1–3 strongly deviating lines (see text).

$^b$ Highest value of the two fitting procedures (FWHM data).

$^c$ Ratio of integrated intensities for a superstructure and a main icosahedral line.

$^d$ Range values measured for five $Al_{16}Mn_{14}$ preparations [9].

$^e$ Calculated for stoichiometric icosahedral composition $Al_{16}TM_{20}$.

$^f$ Data from Ref. [9].

\[
G_0 = \frac{(N + MT)^{1/2}}{Z[2(2 + \tau)^{1/2}]}
\]

\[
G_1 = \frac{[\tau(N\tau - M)]^{1/2}}{Z[2(2 + \tau)^{1/2}]}
\]

\[
\tau = \frac{1 + \sqrt{5}}{2}
\]

where $Z$ denotes the hypercubic lattice parameter and $M$ and $N$ are the Cahn indices. Values of $Z$ were determined for each system, as shown in Section 6.

In as-quenched Al–Cu–Fe, the phonon disorder parameter $A$ (Table 2) is lower by up to an order of magnitude than that of the metastable quenched Al–Mn and Al–Cr i phases, but increases sharply in the sequence Fe < Mn < Cr. The same trend is shown by the parameters derived from FWHM or integral widths.

The phason disorder parameter $C$ lies, for all three Al–Cu–TM systems, in the lower range of values for metastable Al–Mn and Al–Cr phases, with only a slight increasing trend in the sequence Fe < Mn < Cr.

Static phonon disorder in as-quenched Al–Cu–Fe phases is usually considered as "quenching disorder", related to the high cooling rate. However, in our samples, it is seen to show a systematic and strong chemical trend, which requires an explanation in terms of electronic stability factors. Table 2 displays the Hume–Rothery parameter $e/a$ (average number of conduction electrons per atom), as well as the atomic size factor $\lambda = (R_\text{TM}^3/R_{At}^3)^{-1}$ (R is the atomic radius, the average being taken over the TM species). After Inoue et al. [1], the stable i phases are clustered in the $e/a$ range of 1.6–1.8 and in the zone of $\lambda$ values of 0.08–0.10. For lower $e/a$ values, metastable i phases only were reported. It can be seen (Table 2) that Al–Cu–Fe and Al–Cu–Mn are closer to the empirical optimal value $e/a = 1.75$ [1], while Al–Cu–Cr lies close to the limit of the stability range. The atomic size factor $\lambda$ falls in the optimal range for all three compositions investigated.

Thus we can tentatively assign the increasing phonon disorder in the series Fe < Mn < Cr to the evolution of the Hume–Rothery factor $e/a$, which approaches the limit of the stability zone.

5. Superstructure of the 6D hypercubic network

The distribution of the atomic 3D motifs on the sites of the 6D hypercubic lattice can belong to either a simple cubic lattice (P) or an f.c.c. lattice (F). The degree of f.c.c. order was shown [8] to depend in i Al–Cu–TM phases on the nature of the TM, as well as on the annealing treatment performed.

The degree of f.c.c.-type order can be assessed by the intensity ratio of superstructure lines (odd Cahn indices) to regular lines (even indices). In Table 2, this degree was estimated by the ratio of the integrated intensities $(7,11)/(8,12)$.

It can be seen that the Al–Cu–Fe i phase is the best ordered, followed by the Al–Cu–Mn phase. Both phases possess a hypercubic lattice of the F type. For the Al–Cu–Cr phase, a sharp decrease in the f.c.c. order is observed, the 6D lattice being closer to the P type.

6. Hypercubic lattice parameter

The parameter $Z$ of the hypercubic lattice was derived from the experimental $G_0$ values of the $(M, N)$ diffraction lines ($G_0 = 2 \sin \theta/\lambda$) using Eqs. (2a)–(2c).
The Z values for the three Al–Cu–TM alloys are displayed in Fig. 3 vs. the metallic radii of the TM atoms, using the $R_{12}$ values valid for a ligand number of 12 [13]. For Mn, the $R_{12}$ value is 1.268 Å and corresponds to the "normal" metallic valence (six) of Mn. As can be seen in Fig. 3, a continuous dependence $Z(R_{12})$ results for the Cr-, Mn- and Fe-based Al–Cu–TM alloys.

Fig. 3 also displays the Z values determined for Al–TM$_{1}$TM$_{2}$ i phases [9] vs. the average TM metallic radii. Using the Mn radius for valence six, the experimental values for the systems Al–Mn–Fe and Al–Cr–Mn fall close to a unique curve, which also describes the Cr–Co- and Cr–Fe-based systems. This observation suggests a similar, primitive cubic hyperlattice for the above-mentioned i phases. In contrast, using for Mn an atomic radius of 1.30 Å (as in closely packed γ-Mn) causes the Z values for Mn-containing systems to lie on a separate curve.

It should be noted that Mn shows, in different crystallographic modifications, two different $R_{12}$ values: 1.30 Å (corresponding to a metallic valence of 4.5) and 1.268 Å (“normal” metallic valence of six). The first is found in the tetragonally distorted f.c.c. γ-Mn (coordination 12). It is also present in the low-symmetry modifications α- and β-Mn, for the crystallographic positions coordinated by 14–16 neighbours. The second $R_{12}$ value (1.268 Å) is only found for the 12-coordinated atoms in α- and β-Mn. It corresponds to a metallic valence of six, also found in neighbouring elements Cr and Fe, and including d orbitals in the formation of the metallic bond. Thus the i configuration seems to activate the maximum metallic valence (six) of Mn.

The observation that the use of $R_{12}$=1.268 Å for Mn fully rationalizes the Z(R) data (Fig. 3) for Al–Cu–TM as well as Al–TM$_{1}$TM$_{2}$ systems confirms the i surrounding of Mn (generally of TM atoms) by 12 Al. This concept of TMA$_{12}$ icosahedra connected to give Mackay polyhedra underlies the Fowler model of i phases [14].

7. Thermal stability of Al–Cu–TM i phases

Differential thermal analysis (DTA) runs were performed up to 1000 °C in order to check the thermodynamic stability of the i Al–Cu–TM phases. In Al–Cu–Fe, no thermal effects appear up to 885 °C (partial melting temperature). The Al–Cu–Mn sample shows a significant exothermic effect around 526 °C. Annealing the as-quenched material for 3 h at 510 °C resulted in complete crystallization into CsCl-type Al$_{62}$Cu$_{25.5}$Mn$_{2.5}$ and Al$_{6}$Mn-type phases. The exothermic effect must be attributed to the crystallization of the i phase.

DTA runs performed on the Al–Cu–Cr sample displayed no sharp thermal effects up to the partial melting point (782 °C). This agrees with the results of 3 h annealing at 510 °C, which showed that the i Al–Cu–Cr phase remained practically unaffected. The residual CsCl-type crystalline phase is preserved by annealing at this temperature.

Split endothermic effects in Al–Cu–Fe (at 885 and 965 °C) and Al–Cu–Cr (at 782 and 855 °C) suggest incongruent melting processes.

8. Conclusions

As-quenched Al$_{62}$Cu$_{25.5}$TM$_{12.5}$ melt-spun ribbons (TM=Cr, Mn, Fe) comprise a dominant i phase. The corresponding hypercubic lattice is of the F type (f.c.c.) for Al–Cu–Fe, the degree of superstructure f.c.c. order decreasing for Al–Cu–Mn. The Al–Cu–Cr as-quenched i phase is closer to a P-type 6D lattice.

The hyperlattice parameter Z was found to decrease in the order $Z$(Cr) > $Z$(Mn) > $Z$(Fe). This suggests that the Mn metallic radius takes the 1.268 Å value (valence six) rather than the most frequent 1.30 Å value (metallic valence 4.5). This result is corroborated by the evaluation of Z data in Al–TM, TM$_{2}$ systems (TM$_{1}$, TM$_{2}$=Cr, Mn, Fe, Co) [9]. The “normal” metallic valence of six (and the corresponding short Mn radius) is rather an exception, only found in the icosahedrally coordinated sites of the α- and β-Mn modifications. Its presence in the Al–Cu–TM and Al–TM$_{1}$–TM$_{2}$ phases confirms the i surrounding of TM by Al, forming local TMA$_{12}$ icosahedra.
Phonon-type disorder, usually considered as "quenching disorder" is weak in Al–Cu–Fe, but increases in the sequence Fe < Mn < Cr. This chemical trend could be explained by the decrease in the Hume–Rothery e/a factor towards the lower limit of the stability range. The phason-type disorder, indicative of alterations in order, remains in all samples at a moderate level, without a significant chemical trend.

The thermal stability of the samples was checked up to 1000 °C. The Al–Cu–Cr and Al–Cu–Fe samples are stable in this temperature range, conserving their i structure. By contrast, the Al–Cu–Mn i phase crystallizes around 526 °C.

A final observation concerns the compositional field of stable Al–Cu–Fe phases. As reported by Bessière et al. [4], Al_{65}Cu_{25.5}Fe_{12.5} possesses an optimal stability, from the thermodynamic point of view, up to the melting temperature. However, our results hint that a slightly lower Fe concentration in the global composition of the alloy could improve the stability of the i component. Two arguments can be emphasized in this respect.

1) The presence of a β-type crystalline phase Al_{15}Cu_{35}Fe_{15} in the as-quenched samples, whose quantity was shown to increase by a factor of three when the nominal Fe concentration was increased by as little as 0.4 at.%. This behaviour shows that the compositions investigated are on the border of the i field, towards Fe contents which are too high.

2) Annealing the Fe-rich ribbons (Fe_{14.5}) at 600 °C induces a massive crystallization of the sample into the β phase. This shows that, at higher Fe contents, the stability field of the high-temperature β phase extends to at least 600 °C. On the other hand, the same annealing applied to the low-Fe sample (Fe_{12.2}) partially dissolves β into the i phase, showing the stability of the latter at this temperature. This i phase become slightly unstable at 800 °C. It is to be expected that a further reduction of the Fe content, even by a slight amount, would improve the stability of the i phase at 800 °C.

Acknowledgments

We are indebted to the Alexander von Humboldt Foundation for providing us with computer facilities. Our thanks are due to Dr. A. Devenyi for invaluable advice and encouragement.

References