Structural studies of (Al\textsubscript{1-x}Ge\textsubscript{x})\textsubscript{65}Cu\textsubscript{10+j}Mn\textsubscript{25-j} (0\textless x \textless 0.4, 0\textless j \textless 10)

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Abstract

In this paper, we present a systematic structural study on the (Al\textsubscript{1-x}Ge\textsubscript{x})\textsubscript{65}Cu\textsubscript{10+j}Mn\textsubscript{25-j} alloy system. The emphasis of the work is to understand the effect of Ge concentration on the occurrence, growth and morphology of the quasicrystalline phases in the system, as we move from Cu/Mn ratio of 20:15 to 10:25 in order to span the varied electronic behavior (as shown in the literature) of this quaternary system. Throughout the series, coexistence of icosahedral and decagonal phases has been observed. To the best of our knowledge, these are the first observations of their type in the alloy system (AlGe) CuMn.

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1. Introduction

The different kinds of quasicrystals known in literature can be broadly classified into two groups—(a) Al-based and (b) non-Al-based (generally Ti/Zr-based), quasicrystals. The Al (Mn/TM) (Si/Ge) based ternary alloy systems are of particular interest due to the broad composition range over which one can stabilize the quasicrystalline phase and also the availability of a range of magnetic properties in this system. The data in the literature indicate that although high concentration of manganese (Mn>22\%) results in the formation of a dominantly decagonal phase in binary Al-Mn, the addition of Ge or Si (12.5\% to 35\%) results in the formation of the icosahedral phase [1]. It is also interesting to note that alloys with higher Mn concentrations (\geq 25\%\) with about 20\% Ge (or about 30\% Si) show magnetic order [2] concentrated spin-glass behavior [3] with a low moment, relatively high $T_c$ and a high coercivity. On the other hand, alloys with lower Mn content are paramagnetic and normally show a spin-glass behavior [4].

Although various data on the Al(Mn/TM) (Ge/Si) alloy system are available in the literature, no systematic study has been done so far on this system to better understand the varied electronic behavior of this
quaternary system as the metalloid and Mn concentrations are changed simultaneously. In Fig. 1, we have identified various magnetic phases reported in the literature, along with the ternary composition Al_{65}Cu_{20}Fe_{15} on a phase diagram. For the present work, we have chosen a quaternary \((A^{1-x}Ge^xCu^{1+y}Mn_{5-y})_y\) \((0<x<0.4, 0<y<0.4)\) system. This series was selected, considering the fact that one of the major limitations in understanding the effect of quasicrystalline order on electronic or magnetic properties has been the inherent disorder present in these systems [3]. One end of this series \((x=0, y=10)\), therefore, consists of the composition \((AlGe)^{65}(CuMn)^{35}\) that is a well-known F-type icosahedral quasicrystal and the other end \((x=0.4, y=0)\) is a 3DPT type ferromagnetic [2] icosahedral quasicrystal \(Al_{60}Ge_{25}Cu_{10}Mn_{5}\) (see Fig. 1).

Looking at the two end compositions, it is clear that, although at both ends of the chosen series we have \((AlGe)^{65}(CuMn)^{35}\), there is a distinct difference between the two end compositions. The F-type icosahedral phase is expected when the ratio of Cu/Mn is 20:15, whereas for the magnetic 3DPT type ferromagnetic icosahedral quasicrystals at the other end, the Cu content has been significantly replaced by Mn \((Cu/Mn\) now is 10:25), along with a sudden increase in the Ge content. Since our desired goal is to look for a magnetic quasicrystal, we have tried to slowly increase the Mn content, along with the inclusion of Ge in place of Al in the series.

Here, we make a systematic study of the effect of such changing concentrations of Cu/Mn ratio along with the increase in the Ge content (that is expected to give rise to the ferromagnetic/spin-glass behavior in the quasicrystals, as discussed above) on the growth and morphology of quasicrystalline structure in this system. Once the stabilizing aspects are made clear, their effect on various electronic properties, e.g. the electronic and magnetic characteristics will get elucidated. The present work deals with the detailed investigations on the synthesis and formation of quasicrystalline phases in the above-mentioned alloy series. Only a few compositions could be stabilized in the desired quasicrystalline phase. The influence of Ge on the structure and morphology has been studied here. An attempt has also been made to elucidate the effect (if any) of increasing Mn content in the Cu/Mn ratio, along with an increase in Ge content.

It is well known that the metalloids including Ge and Si have special effect on the stability of quasicrystals and their manifestations are found in both icosahedral and decagonal phases. These manifestations are more prominent when Ge is substituted in place of Al. Some examples of the influence of metalloids can be found in the literature [5,6]. In the light of this, it is expected that inspite of variations of other elemental compositions, the influence of variation of Ge concentrations will have the dominant effect on the stability of the quasicrystalline phases in the chosen alloy series \((Al^{1-x}Ge^xCu^{1+y}Mn_{25-y})_y\) \((0<x<0.4, 0<y<0.4)\). Thus, the results on the stability of icosahedral and decagonal phases as a function of Ge concentration are valid at least to the first order of approximation. Further work gauging the influence of Ge on the phase stability of these alloys is being carried out and results will be forthcoming.

The coexistence and the relative growth of the icosahedral and decagonal phases in these two distinct regions of this alloy system have been investigated using the transmission electron microscopy (TEM) techniques in imaging as well as selected area diffraction (SAD) modes.

![Fig. 1. A phase-diagram of (AlGe) Cu Mn alloy system, identifying the main ferromagnetic/concentrated spin-glass quasicrystals reported in the literature along with the F-type Al_{60}Cu_{20}Mn_{15} quasicrystal.](image-url)
2. Experimental

Alloys of (Al$\text{1}_x$Ge$x$)$_{65}$Cu$_{10+y}$Mn$_{25-y}$, were made form the high purity (99.999) (5N) elemental components by rf melting under argon atmosphere. They were then melt spun on a single copper roller rotating with a surface speed of $\approx$ 45 m/s, thereby producing ribbons of f50-Am thickness and 1-3-mm width. The occurrences of phases on as-quenched ribbons were determined using both X-ray diffraction (with Cu Ka radiation) and transmission electron microscopy (TEM). For TEM, the ribbons were electro-polished with a solution of 67% methanol and 33% nitric acid. For the electron microscopic explorations on the structural aspects of the present quasicrystalline alloys, both imaging as well as the diffraction modes of a 100-kV CM-12 Phillips microscope were employed.

3. Results and discussion

X-ray powder diffraction data for all the samples for which the electron diffraction results are discussed later, are shown in Fig. 2a to e. The indexing was done according to the scheme proposed by Bancel and Heiney [7] for icosahedral and Tsai et al. [8] for decagonal. From the XRD results (Fig. 2a to d), it is clear that the intensity of the decagonal peak (10000 1) first increases with the addition of 3 at.$\%$ of Ge and then decreases for samples with higher concentration of Ge as the Mn content is slowly increased to move away from the region of Cu/Mn ratio of 20:15. The decrease of decagonal peak intensity with the increasing Ge content is continued to be observed for the samples with Ge content of $\geq$25 at.$\%$, namely, Al$_40$Ge$_{25}$Cu$_{11}$Mn$_{24}$ (Fig. 2e) and Al$_{42}$Ge$_{23}$Cu$_{13}$Mn$_{22}$ (Fig. 2f). In Fig. 2d-f, the decagonal peak shows up only as a small shoulder along with the icosahedral (110000) peak. These facts probably indicate that increasing Ge content helps to stabilize the icosahedral phase in this series. Such a variation of the

Fig. 2. (a to e) The intensity (in arbitrary units) versus 2h plots (X-ray diffraction) on the (M$_{1-x}$Ge$_x$)$_{65}$Cu$_{10+y}$Mn$_{25-y}$ (0YXV0.40YVYV10) series. Panels (f) and (g) are similar plots for Al$_{53}$Ge$_{22}$Mn$_{25}$ and Al$_{55}$Ge$_{22}$Cu$_3$Mn$_{22}$. 


intensity of decagonal peak with Ge concentration has been studied for the first time. Apart from the icosahedral and decagonal phases, the diffraction pattern in Fig. 2e and f also indicated the presence of a crystalline AlMn phase. It seems that the introduction of very high Ge concentration (f 25 at.%) in the (AlGe) CuMn quaternary system, although stabilizes the icosahedral phase, also introduces a crystalline (non-magnetic) phase. To verify this point, we show the XRD results of Al$_{42}$Ge$_{23}$Cu$_{13}$Mn$_2$ and Al$_{53}$Ge$_{22}$Mn$_5$ (not included in our TEM discussion later) in Fig. 2f and g. On comparison, the presence of AlMn peak can be noticed in both Fig. 2e and f where very high concentrations (f 25 at.%) of Ge and Mn are present along with the Cu (f 12 at.%) in a quaternary system; whereas in Fig. 2g, this peak is missing, although the Ge and Mn contents are almost similar. These results seem to indicate that the icosahedral phase is stabilized in a quaternary system by increasing the Ge and Mn contents to f 25 at.% (later in the paper, this is verified by electron diffraction too!), however, along with this, a crystalline AlMn phase starts appearing.

It has been found [9], that Al$_{65}$Cu$_{25}$TM$_{15}$ quasi-crystals are well ordered when TM=Fe, and there exists the possibility of finding primitive to face centered ordering in these systems when TM=Mn or Cr. Daulton and Kelton [5] have reported that partial replacement of Al by Si (V 5 at.%) in Al$_{65}$Co$_{20}$Cu$_{15}$ quasi-crystals enhances the decagonal phase formation. However, to our knowledge, no detailed systematic structural study exists on the (Al/Ge)$_{65}$Cu$_{20}$Mn$_{15}$ quaternary alloy system. In order to increase the scope of our studies so as to include another kind of quasicrystalline alloy Al$_{40}$Ge$_{25}$Cu$_{10}$Mn$_5$, reported in the literature as an icosahedral quasicrystal with a substantial magnetic moment, we have investigated the more general series of alloys (Ali$^+$Ge$^+$sCu_{10+y}Mn$_{25-y}$ (0$\leq$s$\leq$0.4, 0$\leq$y$\leq$10).

The results of TEM investigations on this series reveal many interesting features. Throughout the series, we find coexistence of icosahedral (I) and decagonal (D) phases. The occurrence, of decagonal phase in the samples of (AlGe) CuMn and especially in the Al$_{60}$Ge$_{25}$Cu$_{11}$Mn$_4$ (x=0.4, y=1), as reported here, are the first studies of their type.

The results of our investigations are described and discussed in the following.

3.1. $x=0$, $y=10$ (Al$_{65}$Cu$_{20}$Mn$_{15}$)

Fig. 3a, b and c shows the SAD patterns from regions rich in the icosahedral phase and illustrate the five-fold, three-fold and two-fold symmetry axes of this phase. Fig. 3d depicts a SAD pattern exhibiting the occurrence of the decagonal phase, the one-dimensional periodicity was found to be 12.5 Å. Fig. 3d shows the micro structure which, in conjunction with the SAD patterns, reveals the coexistence of icosahedral and decagonal phases, the former being the dominant variant. Fig. 3f shows mottled micro structure which in turn suggests the occurrence of phason disorder.

3.2. $x=0.05$, $y=9$ (Al$_{62}$Ge$_3$Cu$_{19}$Mn$_{16}$)

The addition of about 3 at.% of Ge promotes the growth of the decagonal phase. The SAD patterns from the decagonal phase with a periodicity of f 12.5 Å, similar to Fig. 3d were observed. Fig. 4a shows a typical micro structure of this sample that consists of nearly circular crystalline grains with the icosahedral phase on the periphery. Some concentration of the decagonal phase can also be seen (marked by D in the figure).

3.3. $x=0.1$, $y=8$ (Al$_{58.5}$Ge$_{6.5}$Cu$_{18}$Mn$_{17}$)

Increasing the Ge concentration to f 6.5 at.% and decreasing the Cu concentration by about 2 at.% yield alloys where still the evidence of both icosahedral and decagonal phases could be noticed. Typical SAD patterns (as shown above) pertaining to I- and D-phases were observed. Fig. 4b exhibits a diffraction pattern where the decagonal diffraction spots have the strongest intensities but crystal-like periodicities in both the directions are easily discernible; thus, this reports an approximant of decagonal phase. This approximant phase, a peculiar order in D-phase is also observed in some other samples of this series.

3.4. $x=0.2$, $y=6$ (Al$_{52}$Ge$_{13}$Cu$_{16}$Mn$_{19}$)

In this sample, the Ge concentration is increased substantially, while keeping the Cu and Mn concentrations nearly the same. The interesting feature that is
Fig. 3. TEM images of Al$_5$Cu$_2$Mn$_{15}$: (a), (b) and (c) SAD patterns from an icosahedral rich region, showing five-fold, three-fold and two-fold orientations, respectively, (d) SAD pattern exhibiting the presence of the decagonal phase, (e) TEM image of the microstructure revealing the presence of both icosahedral and decagonal phases (with icosahedral being dominant phases) and (f) the microstructural characteristics as observed by TEM technique revealed variable mottled contrast, suggestive of the phason disorder.
Fig. 4. (a) Microstructure showing a crystalline grain surrounded by the icosahedral phase and some concentration of decagonal phase in Al_{62}Ge_{12}Cu_{9}Mn_{16}. (b) Electron diffraction patterns in Al_{58.5}Ge_{6.5}Cu_{18}Mn_{17} from the decagonal region, notice the elongation of spots in (b). (c) The two-fold diffraction pattern of the decagonal phase in Al_{52}Ge_{13}Cu_{16}Mn_{19}. (d) Electron diffraction pattern of crystalline phase present in the sample (an interplanar spacing of 4.38 Å in (111) direction is observed). (e) Rod-like morphology in the same sample.
revealed by TEM here is the strong presence of decagonal phase that is almost unnoticeable in the corresponding XRD for the sample. Fig. 4c shows a two-fold diffraction pattern from a decagonal phase in this alloy. The streaks along the aperiodic direction can be easily seen. The diffraction pattern from a crystalline phase (see Fig. 4d) with an interplaning spacing of 4.38 Å along the (111) orientation is also seen for this sample. This crystalline component is probably a metastable phase that is produced during the quenching process [10] and is not observable from the XRD pattern. The micro structure showing a rod-like morphology for the decagonal phase is shown in Fig. 4e.

3.5. $x=0.39, y=1$ ($\text{Al}_{40}\text{Ge}_{25}\text{Cu}_{1}\text{Mn}_{24}$)

The last sample in the series, with significantly decreased Cu concentration and a large concentration of Ge, exhibits several interesting features. The presence of both the icosahedral and decagonal phases was evidenced in this sample too. In the icosahedral-rich region of the sample, typical SAD patterns of five-fold, three-fold and two-fold symmetries were observed and the decagonal-rich region showed the presence of decagonal phase with a periodicity of 12.4 Å. Fig. 5a is a lattice image of a decagonal phase with a periodicity of 12.4 Å along the direction of the arrow. Fig. 5b and c shows the micro structures from two different grains of this sample; representing typical icosahedral and decagonal phases respectively. Fig. 5c shows a representative microstructure of a superlattice ordered phase; the block structure represented by the broad lattice fringes, repeats after seven fringes, the distance between two consecutive lines being 111 Å. An estimate of typical grain sizes of both icosahedral and decagonal phases present in the samples is made from the microstructures illustrated in Fig. 5b and c. The icosahedral grains are found to be an order of magnitude smaller than the decagonal grains.

Fig. 5. (a) Lattice image of the decagonal phase present ion $\text{Al}_{40}\text{Ge}_{25}\text{Cu}_{1}\text{Mn}_{24}$ (the twin interface of icosahedral and decagonal phases is clearly visible); (b) the micro structure form an icosahedral grain; (c) representative microstructure of a decagonal phase with equiaxed grains.
magnitude larger (2.4 Am) in size as compared to the decagonal grains (f 0.2 Am).

4. Conclusions

From the above discussions, it is clear that both icosahedral and decagonal phases are present throughout the series. It is suggested both by XRD data and the TEM analysis that, generally, the inclusion of Ge in place of Al seems to stabilize and helps to grow the icosahedral phase. It should be noted that in the quaternary system \{(AlGe)65(CuMn)35\} chosen here, the samples with large Ge concentrations (f 25 at.%) along with the Mn concentrations of f25 at.% (reported in the literature as a magnetic quasicrystal) although have large concentrations of icosahedral phase; they also contain significant amount of decagonal phase along with some crystalline Al-Mn phase. As this work clearly brings out, it is important to do the structural verification by TEM, as it is extremely difficult to identify and separate the icosahedral and decagonal phases just from the XRD data (see, e.g. Fig. 2d, which shows almost single phase icosahedral features by XRD, but the TEM data reveal the strong presence of decagonal phases in Fig. 4).

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