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Exploration in the Sc-Al-Cu system: evidence for *i*-$ScAl_{2.4}Cu_{3.2}$ quasicrystal and new crystal data for five intermetallic phases.

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Exploration in the Sc-Al-Cu system: evidence for *i*-$ScAl_{2.4}Cu_{3.2}$ quasicrystal and new crystal data for five intermetallic phases.

The ternary system Sc-Al-Cu system has been investigated in this work. Several alloys with various compositions have been prepared by arc-melting from the elements and studied by X-ray diffraction. An icosahedral quasicrystal of formula $ScAl_{2.4}Cu_{3.2}$ has been identified using the reciprocal space reconstructed from its diffraction images. The diffraction data collected for several single crystals led to solve and refine five crystal structures: cubic $ScAlCu_2$ ($Fm\bar{3}m$), hexagonal $ScAl_{1.1}Cu_{0.9}$ ($P\bar{6}m2$), hexagonal $ScAl_{2.4}Cu_{2.9}$ ($P6_3/mmc$), tetragonal $ScAl_{5.3}Cu_{6.7}$ ($I4/mmm$) and orthorhombic $ScAl_{2.2}Cu_{3.4}$ ($Cmmm$). Almost all these structures are characterized with copper/aluminum atomic mixing at most of the crystallographic sites and the atomic arrangements are favorable to the existence of stoichiometry ranges for the compounds. These results, providing new single crystal data sets for these ternary compounds, clarify and confirm the structures previously reported (from crystal or powder data).

Keywords: intermetallic phases; quasicrystal; crystal structure; aluminium; scandium; copper

Introduction

The numerous compounds that form in the intermetallic systems are characterized with a wide variety of structural arrangements which can be as simple as those found in Laves phases [1, 2] or much more complex as in well-known Bergman-type compounds [3]. Some intermetallic phases even belong to the peculiar family of complex metallic alloys with giant unit cells containing up to thousands of atoms [4, 5]. Such structural complexity is able to have a significant impact on the physical properties of materials [6]. It has been underlined in previous works that the valence electron count per atom (*e/a*) is an important parameter for the description of structures but also for the formation of compounds [7-10]. The electron-poor compounds, namely those having *e/a* ratio lower than 2.0, are characterized by their

relationships to the Hume-Rothery phases [11, 12]. As earlier reported, this family which was initially limited to the different structural types of brass now includes the category of approximant and quasicrystalline compounds [13]. In a paper that describes exploratory syntheses of indium-based compounds, a fast overview has been given on how these electron-poor materials can be reached [10]. Building intermetallic compounds by the use of transition metals in place of *p*-block elements reduces this ratio as achieved for example in the phases $Li_{13}Cu_6Ga_{21}$ (*e/a* = 2.05) [14] or $Mg_{32}Zn_{37}Al_{12}$ (*e/a* = 2.14) [15] that can be described as Bergman-type structures. Very often, quasicrystals are found with very close compositions beside such complex crystalline structures [16], as it is nicely illustrated with coexistence in the alloys of the R-Li_3CuAl_5 approximant and the T-Li_3CuAl_5 quasicrystal (*e/a* = 2.11) [17]. Rationalization has been searched of what are the driving forces that favour the atomic organization in crystalline or quasicrystalline materials, within limits of adaptability of the classical chemical principles as octet rule, Wade-Mingos and Zintl concepts, acid and base notions… [18]. Nevertheless, the long-range propagation of the local icosahedral order, which necessarily implies periodicity, has something to do with chemical frustrations occurring in interactions of various nature within such complex atomic arrangements. It must be pointed out that quasicrystals are often encountered in intermetallic systems but more specifically in those including Mg, Al, Cu, Zn or rare-earth elements as Sc [6, 15, 18-22].

Focusing now on the scandium-copper-aluminium system, the interest of materials lies in the alloy strengthening and the resistance improvement provided by incorporation of Sc in copper aluminides [23]. Promising applications in the development of high strength alloys [23-25] have encouraged some thermodynamic studies presented in ternary diagram reports [26-29]. These works have highlighted the complexity of the system also shown by the various structural reports, more or less incomplete, given in the Pearson crystal data base

[30]. Twenty reports are listed for ternary compounds in the Sc-Al-Cu system (vs. twelve in the alike Sc-Ga-Cu system, with unrelated stoichiometries and crystal structures) of which only five provide finalized structure determinations either from powder or single crystal X-ray diffraction data. Up to now, five structural types have been identified for these ternary compounds. However, significant stoichiometry deviations within a same structural model must be underlined, which leads to uncertainty about the phases existing really in this system. It should be stressed that at the moment this work was initiated, only lattice parameters were known for the orthorhombic structure characterized later [31], the structure of which has been included recently in the Pearson database (2016 update) [30]. At the same time, the new compound $ScAl_{1.98}Cu_{4.02}$ was identified from its powder pattern and its cubic $Im\overline{3}$ structure is described in a paper which enumerates also the older works published on this ternary system [32].

The present work has been carried out with the aim to progress in the knowledge of this system containing complex intermetallic materials that are likely to display interesting specific properties. As any variation, even very weak, in the material composition may induce important structural changes in the final compound [15], it must be crucial to properly identify the compounds, establish their stoichiometries and possibly detect the existence of stoichiometry ranges associated with each structural type. This objective can be reached by the juxtaposition and the confrontation of all the experimental data published in the literature, so that any new experimental data is of interest to better understand phases in this system.

The work reported here brings out the existence of an icosahedral quasicrystal and reports the X-ray structural determination and refinement for seven single crystals in the Sc-Al-Cu system. They belong to five structural types and display either cubic, tetragonal,

orthorhombic or hexagonal symmetry. The stoichiometries of the compounds are determined both by structural refinement and by chemical analyses of single crystals.

Experimental section

Commercial reagents used in this study have been handled in a glove box filled with argon and were taken without special purification treatment. Little pieces of Al (Merck, analysis grade, > 99.95%) were cut from a foil whose surface had been previously cleaned using an acid solution. Small lumps of Sc (Alfa Aesar, 99.9 %) and Cu powder (Merck, analysis grade, > 99.5%) both stored under argon atmosphere were added to make pellets which were later fused in an arc-melting 'home-made' furnace. For each pellet, the total weight of matter was comprised between 1 and 2 grams and the resulting alloy, obtained as a roundish ingot, was molten several times to improve its homogeneity. In all cases, no unusual weight loss was noted at the end of the melting operations. Several alloys have been prepared in this work with various compositions chosen either far or in the vicinity of compositions known for the different structural types. Sometimes, for the best-crystallized alloys, nice well-shaped and easy to separate single crystals have grown on the surface of the ingot, they were primarily chosen for X-ray studies and chemical analyses. Otherwise the ingot has been broken to obtain beautiful and regular crystallized pieces for the characterization.

Within each alloy, the predominance of one crystalline phase could be noticed through the similarity in composition and in diffraction of the various fragments collected and tested. Several crystals taken either from the surface or from the bulk, were examined to identify each compound. The most regular in shape and best-diffracting crystals were checked for singularity and those displaying the required quality for X-ray crystallographic study were chosen for intensity measurement. The intensity data collection was performed on the Xcalibur CCD (Oxford diffraction) four-circle diffractometer using Mo-Kα radiation for all crystals except the

small crystals selected on an ingot prepared with composition ScAlCu, for which intensities were measured on a Bruker D8 Venture diffractometer equipped with an Incoatec IμS 3.0 Mo micro-source (110μm beam) and a Photon II CPAD detector.

The single crystal structures were solved using SHELXS [33] and refined with SHELXL program [33, 34]. Some details on the single crystals, data collection and structural refinements are given in table 1. Full CIF files have been deposited at the Cambridge Crystallographic Data Centre (CCDC) [35] and are freely available with the corresponding CCDC numbers indicated in table 1.

Diffracted intensities were recorded for all the reflections, including symmetry equivalent and redundant ones, within the complete diffraction sphere. They were corrected for absorption effects using the procedures included in CrysAlis or Apex software and merged into final data sets to be used in the refinements. Atomic coordinates and anisotropic displacement parameters were refined for all atoms. Powder patterns were recorded using a Philips analytical X'Pert X-ray diffractometer equipped with a copper tube, a hybrid (parabolic multilayer mirror and two-crystal) monochromator and the Xcelerator detector. Energy-dispersive X-ray spectroscopy (EDX) measurements were carried out for single crystals previously identified, using an Oxford Instrument Environmental Scanning Electron Microscope equipped with an X-Max large area SDD sensor that allows excellent sensitivity, precision and resolution. The chemical analyses were performed using an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) Agilent 7900 equipment.

Results and discussion

A series of alloys was prepared with various compositions spread in the ternary diagram both in the vicinity and further from the compositions characterizing the known structural types. In each of these alloys, nice pieces likely to be single crystals were selected for diffraction data

collection. The results presented here relate to alloys of quite homogeneous composition and whose crystalline quality was sufficient to allow study by X-ray diffraction. However, among the collected X-ray data, an unusual set of data has been identified as that of a quasicrystal whereas seven sets of data correspond to five types of crystals. The symmetry of the structures is found to be hexagonal, tetragonal, orthorhombic and finally cubic gradually as the copper content increases in the compounds. The main information and results are given in table 1 for each of the seven crystal structure refinements. Atomic positions, site occupations and equivalent displacement parameters can be found in supplemental material.

The $ScAlCu_2$ ($Sc_{25}Al_{25}Cu_{50}$) cubic structure

With the higher Cu/Al ratio, the crystals S42 and S45 (isolated from an alloy prepared with $Sc_3Al_2Cu_6$ composition) are characterized in the F$m\bar{3}m$ cubic symmetry (a = 6.19 Å) with three independent positions respectively filled with Sc, Al and Cu atoms. Since the site occupations do not deviate from unity, the refined composition remains close to $ScAlCu_2$ which is in good agreement with the analyses giving 1:1.01:2.08 for the Sc:Al:Cu ratio. This also agrees with the previously reported structure [36]. The refined composition is very close for the two crystals and within standard deviation limits so that the compound must be probably considered as a stoichiometric compound. Note that indexation of the data in a primitive cubic cell of parameter *a*/2 (by missing the very few extra-reflections) would lead to only two atom positions, one for copper and one for an unlikely Sc/Al mixture (proportion converging to fifty-fifty) as was done in old reports [37, 38]. This attests for atomic ordering and lattice doubling when Al is substituted for Cu in the ScCu binary structure (Pm$\bar{3}$m, a = 3.24Å) or Cu substituted for Al in ScAl (Pm$\bar{3}$m, a = 3.38Å).

The $ScAl_{2.2}Cu_{3.4}$ ($Sc_{15.2}Al_{33.3}Cu_{51.5}$) orthorhombic structure

The orthorhombic symmetry was found for the single crystal S37 selected in the $Sc_3Al_9Cu_{15}$ alloy, in which a Cu/Al ratio of 1.56 was measured from EDX analyses of the crystal. They led to a Sc:Al:Cu ratio of 0.9:2.15:3.49 which quite well agrees with the refined composition 1:2.19:3.42. The structure solved and refined in C*mmm* space group (a = 21.82, b = 8.33, c = 8.32 Å) consists in 3 Sc and 13 M crystallographic sites. The complete filling of Sc sites was checked by free refinement of their occupation. All the M positions were considered with atomic Cu/Al mixture except M10 which was finally considered to be filled only with copper. Next, the M2 position was split into very close half-filled positions *4g (x 0 0)* and *8p (x y 0)* which led to a significant improvement in the agreement factors. Finally the occupation was freely refined for this split site with Cu-filling at *4g* and Al-filling at *8p*. The atomic arrangement in $ScAl_{2.19}Cu_{3.42}$ ($Sc_{15.1}Al_{33.1}Cu_{51.7}$) is that of a crystalline approximant, comparable to that of $ScAl_{2.34}Cu_{3.10}$ ($Sc_{15.5}Al_{36.4}Cu_{48.1}$) recently studied from synchrotron X-ray powder data [31]. The polyhedral packing and the approximant-to-quasicrystal relationships have been described in detail for this isostructural compound [31]. Similarities in the two structural solutions are to remark, as the entire Cu-filling of the M10 site and the disorder phenomenon around the M2 position. Nevertheless, substantial differences arise in the atom distribution (Cu and Al) over all the M positions. Obviously, it results from compositional variation (Cu/Al ratio of 1.56 instead of 1.32) but it is important to mention that all sites are not equally affected. This reminds us what was encountered in an another aluminium ternary system for the approximant compound $Mg_{32}Al_{12}Zn_{37}$ and related compositions [15]. Actually, it was shown that specific areas in the atomic packing (the M_{60} outer shell of the Samson's polyhedron for $Mg_{32}Al_{12}Zn_{37}$) are able to accommodate some composition variations, through distortions and disorder phenomena. It is likely that in the current structure of $ScAl_{2.19}Cu_{3.42}$, in addition to structural preferences for the replacement of Cu by Al at specific sites, the

disordered region around M2 split position is the place for adaptation of the structure to the chemical composition. This is also a strong argument for the existence of a chemical composition range for this structural type that incorporates at least $ScAl_{2.19}Cu_{3.42}$, the composition of the current single crystal, and $ScAl_{2.34}Cu_{3.10}$, the composition cited above for a powder sample [31].

The $ScAl_{2.38}Cu_{3.22}$ ($Sc_{15.1}Al_{36.0}Cu_{48.9}$) icosahedral quasicrystal

The S32 sample was a nice and shiny fragment selected as a 'single crystal' from an alloy prepared at $Sc_3Al_{7.5}Cu_{9.5}$ composition. As for other samples, the diffracted intensities were recorded over the complete diffraction sphere. Despite discrete and well defined diffraction spots featuring some long-distance order as can be seen on a characteristic diffraction image (figure 1), the diffraction data collected for this sample could not be properly indexed with three vectors in a three dimensional space. At first, the eventuality of twinning was considered but the problem could not be solved. Then in order to eliminate any twinning and the risk of missing a new phase, some amount of the material was crushed into fine powder to record a powder pattern (given in supplemental material) but its full indexation also remained unsuccessful. Actually, the S32 sample was a single quasicrystalline specimen that gave discrete spots and good quality diffraction images. The complete 3D reciprocal network has been reconstructed from these images using the tools available in Crysalis software. This allowed a subsequent thorough investigation of the symmetry features of the diffraction diagram (figure 2).

The careful examination of the reciprocal network revealed the presence of six 5-fold axes separated by 63.4° together with 2- and 3-fold axes, that are the characteristic signature of an icosahedral quasicrystal [19]. Starting from the network projection along one of the 5-fold axis, specific rotations of 37.6 or 31.7° in the appropriate directions moves to 3-fold and 2-fold projections (figure 2).

As the presence of secondary phases in the alloy could not be totally excluded, the powder was not used for chemical analyses and only well identified (X-ray checking) fragments were analysed. With a large and plane surface, the sample used for the X-ray data collection allowed EDX analyses at several areas that show an extremely low fluctuation in its chemical composition. Analyses carried out for the other specimens also remain in the standard deviation limits. The composition 1.00(3):2.38(8):3.22(8) corresponding to the formula $Sc_{15.1}Al_{36.0}Cu_{48.9}$ (*e/a* = 2.02) was established for the quasicrystal. The existence of a stoichiometry range for this quasicrystalline compound is suggested by the difference in composition with $Sc_{16}Al_{38}Cu_{46}$ ($ScAl_{2.37}Cu_{2.87}$, *e/a* = 2.07) [39] previously reported with its quaternary analogue $Sc_{15}Mg_3Ga_{34}Cu_{48}$ (*e/a* = 2.02) [40] to be a quasicrystal of Tsai-type. It is specified in [39] that quasicrystal ($Sc_{16}Al_{38}Cu_{46}$) also exist in an elongated composition region defined by $Sc_{18+x}Al_{34-x}Cu_{48}$, x = 0 to 2 . Findings of the present work bring additional information about the stoichiometry range in which an icosahedral quasicrystal may form, which should be extended at least to the Cu-richer current composition $Sc_{15.1}Al_{36.0}Cu_{48.9}$.

The significant role of Hume-Rothery's rules and *e/a* ratio as determining factors in the compounds formation has been frequently underlined in the literature, and it was also stressed that the formation of compounds is very sensitive to the chemical composition, see for example in [41]. Thus it is important to point out that compositions of the orthorhombic, quasicrystalline and even tetragonal phases characterized in this work are fairly close, despite *e/a* ratios that take respectively the values 1.96, 2.02 and 2.09. This observation can be a useful element in the understanding of the disorder phenomena that occur in the crystalline atomic arrangements and can be viewed as an intermediate steps towards aperiodicity.

The $ScAl_{5.3}Cu_{6.7}$ ($Sc_{7.7}Al_{40.8}Cu_{51.5}$) tetragonal structure

The diffraction data set collected for crystal S36 (issued from $Sc_3Al_{13}Cu_{15}$ alloy) is characterized by the tetragonal symmetry and the structure was refined in I4/*mmm* space group (a = 8.56, c = 5.01Å) with one Sc, one Cu and two Cu/Al atom positions. Final refinement leads to the stoichiometry $ScAl_{5.34}Cu_{6.66}$ which agrees well with the EDX analysis giving a ratio Sc:Al:Cu of 1:5.0:6.5. The current structure fits that of $ScAl_6Cu_6$, otherwise formulated $ScAl_{8-x}Cu_{4+x}$ [42] and determined from powder data. It has been described with a range of composition from x = 0 to 2.6 which needs to be very slightly extended to 2.66 to incorporate the current compound. Note that the stoichiometry 1:4.3:7.7 was reported for a compound stated (on the basis of its lattice parameters) to be isostructural with $ScAl_6Cu_6$ [43], it also matches the $ScAl_{8-x}Cu_{4+x}$ formula with x = 3.7, a value well outside the given composition range.

The $ScAl_{2.4}Cu_{2.9}$ ($Sc_{15.9}Al_{38.1}Cu_{46.0}$) hexagonal structure

From its diffraction data, the sample S35 was rapidly identified as a twinned crystal. Since no more than 2% of the diffraction spots overlap, the reflection data could be easily extracted. Moreover, an additional data set characteristic of a single crystal was collected from sample S34 extracted from the same alloy (prepared at the composition $Sc_3Al_2Cu_6$). Structure was solved and refined from both data sets (S34 and S35) within the $P6_3/mmc$ symmetry and refined with one Sc and 6 Cu/Al independent positions. The presence of a rather short distance of 2.22Å between two positions (M5 and M6 sites) could be the sign of an incorrect space group or an inappropriate lattice. Therefore the indexation and profile refinement of a powder pattern (given in supplemental material) recorded for the alloy were used to eliminate any doubt about the lattice dimensions. On the other hand, trials to solve and refine the structure in lower symmetry space groups remain unsuccessful to solve this problem, these short contact always

subsists even in P1 space group. Another major question relative to these positions raised during the final steps of the structural refinement. Very close R1 values were obtained for several combinations of the atomic distribution (Cu and Al) at M5 and M6 sites, making rather difficult the choice between the different options. Modelling an uncomplete filling together with an atomic mixing is not easy to parametrize, so several refinements were carried out using various atom combinations at these positions. This rapidly led to reject the exclusive presence of Al at these two sites, which gave unrealistic refinement results. It therefore remained to consider either Cu or a mixture of Cu and Al at each of these sites. All these refinements converged to the same agreement factor. Interestingly, changes at these two positions have only very small impact on the Cu/Al proportions at all the other sites. Depending on the nature of atoms at M5 and M6, the global Cu/Al ratio varies between 0.9 and 1.2 corresponding respectively to the formulas $ScAl_{2.72}Cu_{2.50}$ and $ScAl_{2.43}Cu_{2.90}$. Curiously, a $P6_3/mmc$ lattice having the same dimensions was assumed for a compound of formula $ScAl_{2.3}Cu_{2.7}$ reported in the literature without any structure determination [36, 44]. Furthermore chemical analyses performed for several crystals previously identified by X-ray were greatly useful for the final decision, almost exclusively giving a Cu/Al ratio slightly higher than unity. Finally, with Cu/Al mixing at M5 and M6 sites, the refined stoichiometry converges to $ScAl_{2.4}Cu_{2.9}$ for each of the two crystal data sets, a formula which fits well the EDX analyses. However, the hypothesis of the existence of a composition range for this compound cannot be totally rejected since this hexagonal structure displays some ability (especially at the two positions discussed above) to accommodate fluctuations in the chemical composition.

The $ScAl_{1.1}Cu_{0.9}$ ($Sc_{33.3}Al_{36.7}Cu_{30.0}$) hexagonal structure

An $MgZn_2$-type hexagonal structure with lattice dimensions a = 5.0, c = 8.2Å was earlier reported in 1966 [37] for a powder of composition ScAlCu. It was characterized with three

sites, one filled by Sc and two by a Cu/Al mixture (50/50). Thirty years later, a compound $ScAl_{1.75}Cu_{3.75}$ was mentioned to display the P6/*mmm* symmetry and the same lattice [44]. In another report submitted by the same group of researchers, the same compound was described in a larger cell with its *c* parameter multiplied by 2.25 (a = 5.0, c = 18.4 Å) but in both cases no structure refinement was provided [45]. The trials to obtain crystals at this composition carried out in the present work did not succeed, pieces with the required quality for an X-ray study cannot be found in the prepared materials yet having a crystalline aspect.

Contrarily, for the alloy prepared at the equimolar 1:1:1 stoichiometry, small individualized crystals have grown inside and in particular on the top of the ingot. They all displayed the hexagonal symmetry and lattice parameters close to those initially reported for ScAlCu [37]. For the two crystals S6 and S7 used for the full X-ray diffraction data collection, the reflections were indexed within hexagonal axes a = 5.22, c = 8.44 Å. The structure was found and refined in the hexagonal $P6_3/mmc$ symmetry with one Sc site and two M sites complementarily filled with Cu and Al atoms leading to the formula $ScAl_{1.12}Cu_{0.88}$. Trying to properly identify the symmetry, refinements (for each of the two crystals) were carried out in parallel in many other possible space groups. Very close R1 agreement factors of respectively 1.37, 1.40, 1.33, 1.33, 1.33, 1.38 and 1.44 are reached in $P6_3mc$, $P\bar{6}m2$, $P\bar{6}2c$, $P6_322$, $P\bar{3}1c$, P31c and P312 against 1.37 in the highest $P6_3/mmc$ symmetry. Whatever the space group, the free refinement of occupation factors seems to show an uncomplete filling of the Sc sites and leads to an improvement in the agreement factors. In such conditions with the Cu/Al proportions allowed to vary, the refined formula comes close to $ScAl_{1.6}Cu_{0.7}$. A comparison is then needed with the $MgNi_2$-type structure ($P6_3/mmc$) given for the compound $ScAl_{1.4}Cu_{0.6}$ described with 2 Sc and 3 Cu/Al positions per unit cell [44, 45]. The possibility of doubling a parameter was subsequently investigated by indexing the reflections in a 1×1×2 supercell of

dimensions a = 5.22, c = 16.88 Å. Note that the resulting *c* parameter is 10% lower than that mentioned above for $ScAl_{1.75}Cu_{3.75}$ and differs only by 0.3 Å from that of $ScAl_{1.4}Cu_{0.6}$. Surprisingly, no structure solution could be found in the $P6_3/mmc$ space group and trials to refine the data with the structural model given for $ScAl_{1.4}Cu_{0.6}$ did not converge. Instead, the structural solutions found in $P\bar{6}c2$ and $P\bar{6}m2$ and refined with free site occupation for Sc atoms respectively converged to formulas (R1 factors) $ScAl_{1.76}Cu_{0.61}$ (2.4) and $ScAl_{1.75}Cu_{0.61}$ (2.2). The structure of crystals S6 and S7 is clearly different from that of $ScAl_{1.4}Cu_{0.6}$ whether the basic cell or the supercell is considered. Contrarily to the structural arrangement in $ScAl_{1.4}Cu_{0.6}$ which derives from that in ScAlCu by shifting the successive layers by *a*/3 (figure 3), the arrangement for the current compound in the supercell can directly be obtained from the basic cell by periodicity, disregarding the atomic proportions at mixed sites. Nevertheless, the only distribution of Cu and Al atoms at the different positions may cause doubling of the parameter. Of course some subtle differences may occur in the proportions at each site accordingly with the symmetry and it is really hard to know without any doubt, what is the better choice for the description of this structure.

At this stage, a thorough examination of the reflection data sets was unavoidable. Although the behaviour is similar for S7, the priority has been given to S6, the best data set with higher intensities. Considering the most probable $P\bar{6}m2$ symmetry, the 19037 recorded reflections are merged into 1553 unique reflections of which 1142 are observed according to the criterion $I > 3\sigma(I)$. Among the observed reflections, 405 with $l = 2n+1$ display a maximal $I/\sigma(I)$ value of 64 instead of 246 for the 737 reflections with $l = 2n$, a difference in intensity which eliminates a $\lambda/2$ contamination of the data [46 and references cited in]. This result gives a strong argument to describe the structure in the supercell with the $P\bar{6}m2$ symmetry.

In order to determine the true composition of the compound, several crystals were taken at the bottom of the ingot and, due to their extremely small size, gathered to be analysed using the ICPMS technique. The measured Sc:Al:Cu ratio is 1:1.12(3):0.99(3) for the three samples and well agrees with the stoichiometry refined with entirely filled Sc positions. It is likely that the agreement factor lowering, noticed when uncomplete filling was considered at Sc sites, solely results from an artificial compensation by adjustment of the Cu to Al ratio at each position. The structure of $ScAl_{1.1}Cu_{0.9}$ is finally given in the supercell with the $P\bar{6}m2$ symmetry. This compound, close to the 1:1:1 composition, could be considered as a line compound with possibly a relatively narrow stoichiometry domain.

The polyhedra and the structural packing

All the structures determined and refined in this work display quite complex atomic three-dimensional arrangements. Except for the cubic phase ScAlCu in which Cu and Al have each their own positions, statistical Cu/Al atomic mixtures with different ratios are found at almost all the crystallographic sites. This could be a mark that, in these structures, copper and aluminium atoms can substitute each other on their positions without too much impact on the whole structural arrangement. This provides the atomic structures with a certain ability to adapt to different chemical compositions and gives arguments to support the existence of composition ranges for the phases.

Although the different $ScCu_xAl_y$ ternary phases studied in the current work are characterized with quite different atomic arrangements and symmetries, they can be considered as three dimensional networks made by packing of polyhedra, namely the coordination polyhedra built around Sc atoms (at 2.85 - 3.08Å) which will be named in the following by using an endohedral notation.

Such a description has been recently given for the cubic compound $ScAl_{1.98}Cu_{4.02}$ in which Sc lies inside a 16-vertex polyhedron displaying 18 triangular, 2 square and 1 pentagonal faces [32]. Each $Sc@Cu_3Al(Cu/Al)_{12}$ polyhedron shares a triangular face with each of its ten neighbours so as their pentagonal faces form a dodecahedral cavity. Disordered copper tetrahedra (two orientations) are located inside this cavity around the origin (and centre) of the I-centred cubic lattice (figure 4b).

The cubic $ScAlCu_2$ 'ordered' compound stands out from all the other compounds because Cu and Al atoms are orderly distributed in the structure. It can be described as a close-packing of *f.c.c.*-type, of rhombic dodecahedra built with Cu and Al atoms at distances from 2.68 to 3.10 Å around Sc atoms. The $Sc@Cu_8Al_6$ polyhedra share all their faces with twelve homologues, six are in the same plane perpendicular to the 3-fold axis of the unit cell, three are above and three below (figure 4a).

In the tetragonal $ScAl_{5.34}Cu_{6.66}$ structure, Sc atom lies inside a 20-vertex polyhedron composed with 8 Cu and 12 Cu/Al atoms at distances ranging from 2.96 to 3.27 Å. These $Sc@Cu_8(Cu/Al)_{12}$ polyhedra display 32 triangular and 2 square faces, they are positioned at the origin and at the centre of the cell so as they share all their Cu vertices with eight homologues, four of which located above and four below (figure 4c).

More complex are the polyhedra observed in the $ScAl_{2.4}Cu_{2.9}$ hexagonal phase with Sc atom placed inside a 15-vertex unit displaying 16 triangular and 2 square faces. This $Sc@(Cu/Al)_{15}$ unit is fused with two homologues through large pentagonal faces giving triple polyhedral units of formula $Sc_3@(Cu/Al)_{45}$ that are close-packed (*h.c.p.*-type) along the *c*-axis of the hexagonal lattice (figure 4e). Such packing is achieved through triangular face sharing (18 shared faces per unit) with the surrounding alike units of which six are in the same plane, six above and six below.

In the orthorhombic structure of $ScAl_{2.2}Cu_{3.4}$, each of the three independent Sc atoms is surrounded by its specific shell of atoms at distances comprised between 2.80 to 3.16 Å. The different types of coordination polyhedra are represented in figure 5. Around atom Sc3, two copper and 14 mixed atoms form a 16-vertex polyhedron $Sc@Cu_2(Cu/Al)_{14}$ displaying 22 triangular and 1 square faces as shown in figure 5. The situation is a little bit more complicated for the coordination shells around Sc1 and Sc2 atoms due to the split M2 position. A 16-vertex unit $Sc@Cu_2Al_2(Cu/Al)_{12}$, slightly different from the previous one, is built around Sc1 atom when M2 is an Al atom at the *8p* site (Al2) and displays one hexagonal, 18 triangular and three square faces. Instead, when M2 is a Cu atom at the *4g* site (Cu2), the coordination polyhedron around Sc1 is a 15-vertex open unit of formula $Sc@Cu_3(Cu/Al)_{12}$ with an hexagonal, 3 square and 16 triangular faces. As another consequence of disorder at the M2 position, the polyhedra around Sc2 are also of two types. A 17-vertex polyhedron of formula $Sc@Cu(Cu/Al)_{16}$ is built with 20 triangular and 5 square faces for a Cu atom at *4g* position. Alternatively when Al2 occurs at *8p* site, a 18-vertex polyhedron $Sc@Al_2(Cu/Al)_{16}$ displaying one square and 22 triangular faces is formed around Sc2 atom. The polyhedral arrangement in the unit cell is represented in figure 4d in which the coordination polyhedra around independent Sc1, Sc2 and Sc3 are represented with green, orange and pink colours, respectively. The variants of polyhedra around Sc1 and Sc2, whose distribution is statistical in the unit cell and whose proportion depends on the M2 site filling by Cu or Al, are not differentiated in the drawing.

Arrangement in the hexagonal compound close to the equimolar composition somewhat differs from others by the nature of Sc coordination polyhedra. In fact, Frank-Kasper polyhedra (truncated tetrahedral $Sc@(Cu/Al)_{12}$ with 4 triangular and 4 hexagonal faces) are built with the Cu/Al atoms placed at ~3.05 Å, they are close packed in a 3D network by sharing all their faces with neighbouring analogues (figure 4f). Extending the coordination shell up to 3.21 Å around

the Sc atoms, this coordination polyhedron is complemented with 4 Sc atoms and transformed into a 16-vertex icosioctahedron with 28 triangular faces of formula $Sc@Sc_4(Cu/Al)_{12}$. However, the structure becomes difficult to describe using these latter units because each Sc atom at the polyhedron surface is also the centre of an analogous nested unit, as shown at the bottom of figure 4f.

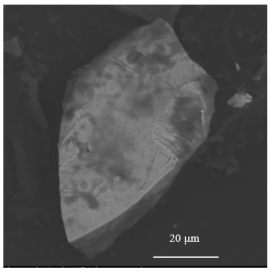
Concluding remarks

The current investigation in the Sc-Al-Cu system has led to discover the existence of the icosahedral quasicrystal $ScAl_{2.38}Cu_{3.22}$ from the record of its diffraction data. This experimental study shows the complexity of this ternary system where periodic or aperiodic structural arrangements occur for close compositions. In addition five structures, determined and refined from new diffraction data sets collected for single crystals in the present work, confirm the literature results. The atomic mixing found for almost all compounds and the comparison with already reported compositions for each structural type bring some insights for better understand this system and particularly for consider composition ranges (stoichiometry domains) for several phases. The case of the hexagonal compound close to equimolar stoichiometry has been discussed more in detail. A structural description in terms of three-dimensional polyhedra packing (coordination polyhedra around Sc) has been used to better visualize the differences between the various atomic arrangements.

Acknowledgements: The author would like to address grateful thanks to Claude Belin, now retired from CNRS, for his contribution to this work.

Table 1. Structural data for $ScAl_xCu_y$ crystal compounds. Note that for *i*–$ScAl_{2.38}Cu_{3.22}$ QC, the calculated ratio Cu/Al is 1.35 and *e/a* is *2.02*.

Formula	**$ScAl_{1.1}Cu_{0.9}$**		**$ScAl_{2.4}Cu_{2.9}$**		**$ScAl_{5.3}Cu_{6.7}$**	**$ScAl_{2.2}Cu_{3.4}$**	**$ScAlCu_2$**	
Alloy comp.	$Sc_3Al_3Cu_3$		$Sc_3Al_8Cu_8$		$Sc_3Al_{13}Cu_{15}$	$Sc_3Al_9Cu_{15}$	$Sc_3Al_2Cu_6$	
Sample ref – CCDC N°.	S6 1913796	S7 1913827	S35 1913826	S34 1914226	S36 1914171	S37 1914172	S42 1914173	S45 1914170
Refined formula	***$ScAl_{1.12}Cu_{0.88}$***	***$ScAl_{1.13}Cu_{0.87}$***	***$ScAl_{2.44}Cu_{2.88}$***	***$ScAl_{2.43}Cu_{2.91}$***	***$ScAl_{5.34}Cu_{6.66}$***	***$ScAl_{2.19}Cu_{3.42}$***	***$ScAl_{1.03}Cu_{2.00}$***	***$ScAl_{0.97}Cu_{2.00}$***
Cu/Al – *e/a*	0.777 – *1.74*	0.769 – *1.75*	1.180 – *2.09*	1.197 – *2.08*	1.247 – *1.97*	1.561 – *1.96*	2.000 – *1.99*	2.062 – *1.99*
Z	4		6		2	16	4	
System **Space group**	hexagonal $P\bar{6}m2$ (187)		hexagonal $P6_3/mmc$ (194)		tetragonal $I4/mmm$ (139)	orthorhombic $Cmmm$ (65)	cubic $Fm\bar{3}m$ (225)	
Lattice (Å)	5.2237(5) 16.8872(3)	5.2215(1) 16.8861(4)	8.4920(5) 8.8714(6)	8.4928(2) 8.8743(2)	8.5606(3) 5.0061(3)	21.8869(7) 8.3311(2) 8.3239(2)	6.1958(6)	6.1976(2)
Volume ($Å^3$)	399.07(8)	398.71	554.04(8)	554.34(2)	366.86(3)	1517.80(7)	237.84(7)	238.05(2)
Crystal size (mm)	0.03×0.04×0.07	0.03×0.06×0.06	0.06×0.07×0.09	0.05×0.09×0.12	0.06×0.07×0.10	0.04×0.08×0.10	0.09×0.14×0.27	0.07×0.12×0.14
μ (mm^{-1})	12.74	12.67	16.05	15.94	20.34	20.86	20.42	20.42
θ range (°)	2.42 – 47.87°	2.41 – 59.62	3.59 – 32.43	2.77 – 32.53	3.37 – 32.63	3.07 – 32.59	5.70 – 32.55	5.70 – 31.70
Ext. coeff ($\times 10^{-4}$)	–	–	0.0034(11)	0.0035(4)	0.0047(7)	–	–	–
Unique reflections	1553 [R_{int} = 2.19]	2387 [R_{int} = 6.66]	1082 [R_{int} = 4.71]	412 [R_{int} = 2.64]	218 [R_{int} = 4.73]	1561 [R_{int} = 4.46]	39 [R_{int} = 5.92]	38 [R_{int} = 4.75]
Atom sites M = Cu/Al mix.	Sc – 2×(*2g, 2h*) M – *6n, 3k, 3j, 2×(2i)*		Sc – *6h* M – *2a, 2b, 4f, 6g, 6h, 12k*		Sc – *2a* M – *8i, 8j* Cu – *8f*	Sc – *4g, 4i, 8o* M – *4f, 4g, 4i, 4k, 4l, 8o* 2×(*4h,8p,16r*) Cu – *8q*	Sc – *4a* Al – *4b* Cu – *8c*	
GoF (on F^2)	1.240	1.184	1.002	1.141	1.107	1.173	1.290	1.456
R1/wR2 [I > 2σ(I)]	0.0243/0.0516	0.0501/0.0851	0.0344/0.0663	0.0329/0.0671	0.0264/0.0644	0.0475/0.1350	0.0167/0.0476	0.0157/0.0488
R1/wR2 (all data)	0.0456/0.0621	0.1012/0.1038	0.0560/0.0698	0.0349/0.0681	0.0272/0.0648	0.0560/0.1478	0.0167/0.0476	0.0157/0.0488
Δρ (e. $Å^{-3}$)	2.14/-2.31	4.80/-3.92	2.87/-1.59	3.33/-1.61	2.18/-1.07	1.48/-0.97	1.34/–0.44	0.31/-0.74



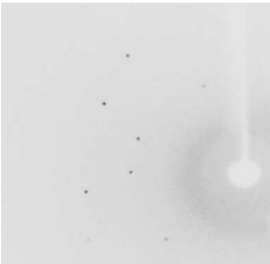


Figure 1.

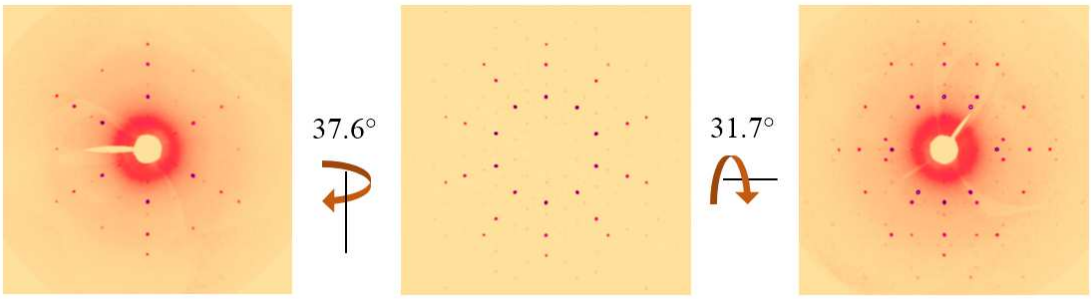


Figure 2.

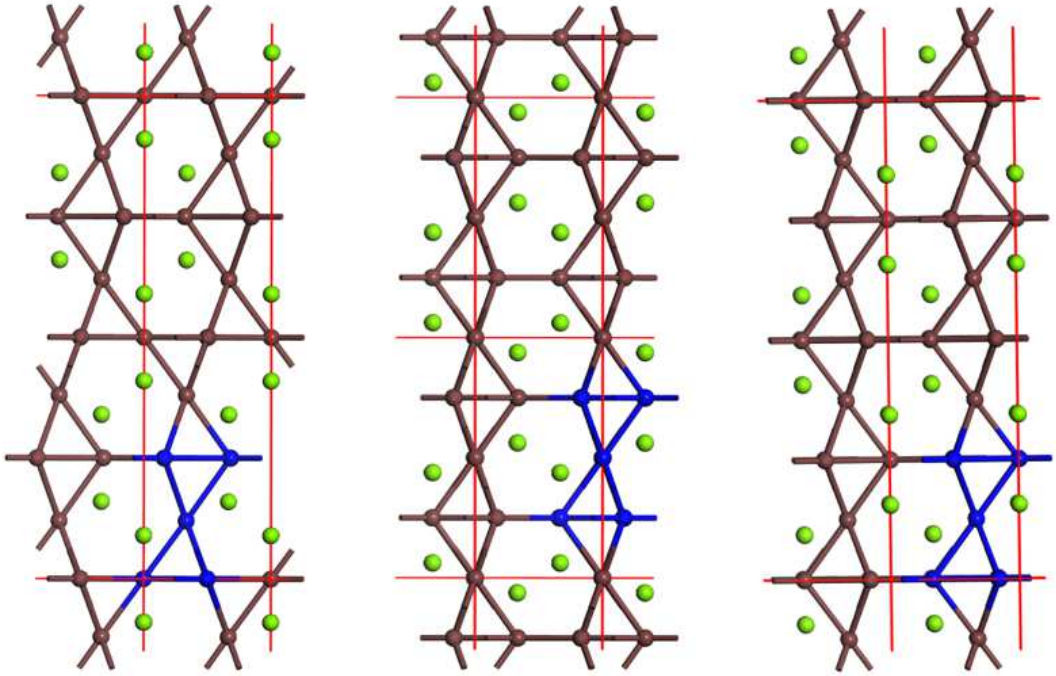


Figure 3.

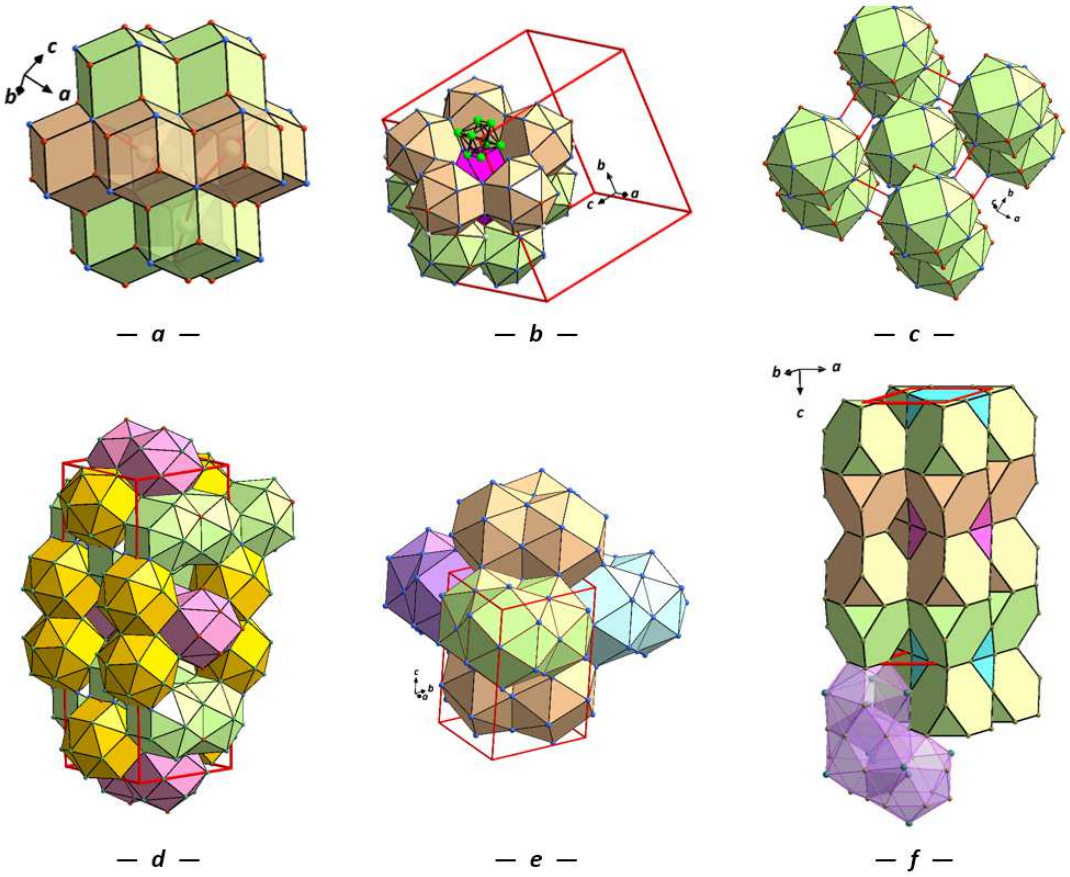


Figure 4.

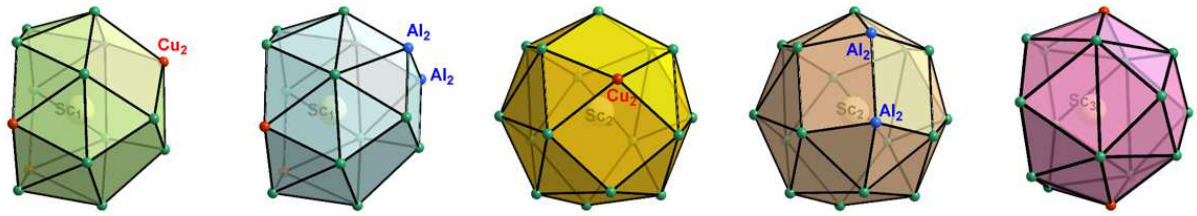


Figure 5.

Figure captions:

Figure 1. The quasicrystalline fragment of $ScAl_{2.38}Cu_{3.22}$ and a typical diffraction image

Figure 2. The reconstructed reciprocal network for $ScAl_{2.38}Cu_{3.22}$ viewed projected along the 3-fold (left), 5-fold (middle) and 2-fold (right) axes. The transition from one to another is possible by specific rotations (well defined angles) of the 3D network.

Figure 3. The hexagonal structures of $ScAl_{1.4}Cu_{0.6}$ ($P6_3/mmm$), ScAlCu ($P6_3/mmm$) and $ScAl_{1.1}Cu_{0.9}$ ($P\bar{6}m2$) viewed along *b*-axis (vertical *c*-axis). Cu/Al sites are not differentiated and a fragment drawn in blue can be used as a landmark.

Figure 4. Structures seen as 3D arrangements of coordination polyhedra built around Sc atoms. Unless indicated otherwise, colours are only used to facilitate the visualization. a - $Sc@Cu_8Al_6$ in $ScAlCu_2$ ($Fm\bar{3}m$), b - $Sc@Cu_3Al(Cu/Al)_{12}$ in $ScAl_{1.98}Cu_{4.02}$ ($Im\bar{3}$), c - $Sc@Cu_8(Cu/Al)_{12}$ in $ScAl_{5.3}Cu_{6.7}$ ($I4/mmm$), d - $Sc@Cu_2Al_2(Cu/Al)_{12}$ or $Sc@Cu_3(Cu/Al)_{12}$ (green), $Sc@Cu(Cu/Al)_{14}$ or $Sc@Al_2(Cu/Al)_{14}$ (orange), and $Sc@Cu_2(Cu/Al)_{14}$ (pink) in $ScAl_{2.2}Cu_{3.4}$ ($Cmmm$), e - $Sc@(Cu/Al)_{15}$ in $ScAl_{2.4}Cu_{2.9}$ ($P6_3/mmc$), f - $Sc@(Cu/Al)_{12}$ in $ScAl_{1.1}Cu_{0.9}$ ($P6_3/mmc$) or alternatively nested $Sc@Sc_4(Cu/Al)_{12}$ represented in violet at the bottom of the drawing.

Figure 5. The Sc coordination polyhedra in $ScAl_{2.2}Cu_{3.4}$ ($Cmmm$). From left to right : the 15-vertex $Sc@Cu_3(Cu/Al)_{12}$ (green, when M2 is copper) or the 16-vertex $Sc@Cu_2Al_2(Cu/Al)_{12}$ (blue, when M2 is aluminium) around Sc1, the 17-vertex $Sc@Cu(Cu/Al)_{16}$ (orange, when M2 is copper) or 18-vertex $Sc@Al_2(Cu/Al)_{16}$ (beige, when M2 is aluminium) around Sc2 and the $Sc@Cu(Cu/Al)_{14}$ (pink) around Sc3..

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