Structure analysis of complex metallic alloys in the Eu-Ag-In system by X-ray diffraction

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Abstract. In this work we investigate the complex atomic structures of two CMAs in the Eu-Ag-In system, these are quasicrystal approximants and their structures are similar to those of the 1/1 and 2/1 approximants found in the Yb-Cd system. The similarities between the Yb-Cd and Eu-Ag-In systems indicate that the RE-Ag-In systems in several ways can be treated as pseudo-binary. The investigated phases however also show some interesting differences; when Cd is replaced by the elements Ag and In partial chemical disorder is introduced into the system. As a response, the positional disorder which is usually observed in certain atomic positions for these types of approximants tends to disappear. The complete structures refined from single crystal data are described in detail and the differences with other related phases are highlighted. The 2/1 approximant in the Eu-Ag-In system is the first to exhibit such a degree of structural perfection in terms of positional order, a feature which makes this phase very suitable for further studies of chemical order and also can give insight into the local structures of related disordered phases. Electron diffraction studies on the 1/1 approximant phase have previously shown the presence of weak superlattice reflections, indicating a superstructure similar to that of the related phase Eu4Cd25. However, no superlattice reflections could be observed by single crystal diffraction and it is thus concluded that the phase has a disordered average structure with possible short to medium range superlattice ordering.

1. Introduction

Complex Metallic Alloys or CMAs for short are characterized by very large unit cells and the presence of well-defined atomic clusters. Quasicrystals are an intriguing subgroup of CMAs that possess long-range atomic order but no periodicity in 3-dimensional space. Conventional methods of structure determination based on X-ray diffraction techniques rely on the prerequisite of lattice periodicity, thus quasicrystals have represented a challenging problem for crystallographers from the very beginning.
Another group of CMAs which are directly related to quasicrystals are their so-called approximants. These are periodic materials in the traditional sense and are related to the corresponding quasicrystals in several ways; mainly they contain the same kind of atomic clusters but in a periodic arrangement. Approximant structures furthermore have strict mathematical relations to the parent quasicrystal, these will restrict the designation (1/1, 2/1 etc.), cell parameters and the symmetry of a specific approximant.[1] Approximants play an important role for understanding the atomic structures of related quasicrystals, since their structures can be determined by conventional X-ray diffraction techniques.

The phases investigated as part of this work are two different approximants in the Eu-Ag-In system. These approximants are related to the family of quasicrystals and approximants in the Yb-Cd system, where the first stable binary icosahedral quasicrystal was found.[2] The typical cluster structure of Yb-Cd type approximants and quasicrystals is displayed in figure 1 a-e. There are two known Yb-Cd type approximant structures; 1/1 YbCd₆ and 2/1 Yb₁₅Cd₇₆, they contain essentially identical atomic clusters but in two different periodic arrangements, as seen in figure 2 a and b.[3-5] Similar approximant structures are known to form in all the binary RE-Cd systems and also ternary systems by replacing Yb by other Rare Earth (RE) elements and Cd by pairs of other elements such as Ag-In, Au-Sn etc.[6, 7] A complete structure model that could be refined against experimental X-ray data was recently obtained for the binary Yb-Cd quasicrystal which serves as a prototype for all the related ternary phases.[8] However, the related ternary phases often suffer from chemical disorder as a consequence of their ternary nature. Although the title compounds naturally show many similarities with the parent phases in the Yb-Cd system there are also several important differences that will be discussed in detail. The initial strategy for synthesising RE-Ag-In approximants involved the replacement of Cd in the parent RE-Cd approximants by half amounts of Ag and In. In the RE-Cd systems 1/1approximants generally form with the stoichiometry RECd₆, thus the corresponding phases in the RE-Ag-In system were prepared with the stoichiometries REAg₃In₉. It has been noted experimentally however, that several ternary approximants have deviating compositions. For example, the ideal composition for the 1/1 approximant in the Yb-Ag-In system is Yb₁₄Ag₄₇In₃₉. This already implies that the phase does not form by substituting Cd by Ag and In atoms statistically distributed over the Cd sites in the structure. It would appear that certain atomic sites have a preference for either Ag or In.[9] This chemical order can however not be analysed using standard X-ray diffraction techniques due to the negligible difference in scattering power between Ag and In at conventional wavelengths.

The purpose of the present study was thus to investigate the effect that the replacement of Cd by Ag and In would have on the superstructure of the 1/1 Eu₄Cd₂₅ approximant and to study the atomic structure of the 2/1 approximant in the Eu-Ag-In system. Other authors have observed superlattice ordering by TEM in the 1/1 Eu-Ag-In approximant that arises as a 2a×2a×2a doubling of the basic cubic cell, and has an F-centred lattice.[12] This is completely in accordance with the refined superstructure of the 1/1 Eu₄Cd₂₅ approximant.
2. Experimental

Reaction mixtures of high purity metals with the relative compositions Eu$_{16}$Ag$_{42}$In$_{42}$ for the 1/1 approximant phase and Eu$_{15}$Ag$_{42.5}$In$_{42.5}$ for the 2/1 approximant were mixed in stainless steel ampoules and sealed by arc-welding in argon atmosphere. The ampoules were then inserted into an electric muffle furnace and then kept at 1273K for 1h followed by annealing at 823K for 72 h and subsequent slow cooling to ambient temperature inside the furnace. Although the samples contained substantial amounts of the target phases, powder patterns could confirm the presence of unknown impurities in the samples. Other investigations show that the ideal Ag:In composition ratios generally deviate from 1:1 in several RE-Ag-In approximant phases, which tend to be richer in Ag.[6] This most likely accounts for the observed impurities in the reaction products. All reaction products were initially identified by powder X-ray diffraction (M03XHF, Mac Science). Single crystal data were collected on a Rigaku R-axis Rapid II single crystal diffractometer operated at 50 kV, 40 mA with MoKα radiation and graphite monochromator. Indexing and empirical absorption correction was performed using the included Rigaku software package. All Ag/In atoms were refined as Cd, since the difference in scattering power between these elements is negligible at the wavelength used for the data collection. The program JANA2006 was used for the structure refinements.[13] The structures were visualized using the programs VESTA 2.0.1 and Caligari Truespace 7.51.[14, 15].
3. Results and Discussion

Crystallographic data for the 1/1 and 2/1 Eu-Ag-In approximant phases are shown in table 1 and refined atomic parameters for the 1/1 and 2/1 approximants respectively in table 2 and table 3.

| Refined comp. | Eu(Ag/In)$_{0.268}$ | Eu$_{13}$(Ag/In)$_{79}$ |
|---------------|---------------------|---------------------|
| Coll. Temperature [K] | 298 | 298 |
| Space group | Im-3 | Pa-3 |
| Lattice const. $a$ [Å] | 15.6222 | 25.2823 |
| Cell volume [Å$^3$] | 3812.6 | 16160.3 |
| $Z$ | 24 | 8 |
| Calc. Density [gcm$^{-3}$] | 8.9505 | 8.921 |
| Abs. Coeff. $\mu$ [mm$^{-1}$] | 30.133 | 30.169 |
| Indep. Refl. | 817 | 8236 |
| Indep. Refl. Obs.[$I > 3\sigma(I)$] | 754 | 4413 |
| $R_{int}$ (obs/all) | 12.73 / 12.81 | 9.54 / 13.12 |
| Parameters | 56 | 338 |
| $R_1/wR_2$ (obs) | 2.51 / 7.47 | 4.73 / 8.53 |
| $R_1/wR_2$ (all) | 2.88 / 7.65 | 12.29 / 9.82 |
| GOF on $F^2$ (obs/all) | 1.79 / 1.76 | 1.95 / 1.62 |
| $\Delta \rho_{min}, \Delta \rho_{max}$ [e/Å$^3$] | -1.45 / 3.51 | -4.59 / 6.22 |

Table 1. Crystallographic data for the Eu-(Ag/In) 1/1 (left column), and 2/1 (right column) approximants. Mixed Ag/In positions were refined as Cd.

| atomic position | occupancy | x | y | z |
|-----------------|-----------|---|---|---|
| Eu1             | 1         | 0 | 0.29782(3) | 0.18656(3) | 0.01368(18) |
| (Ag/In)$_1$     | 0.395(7)  | 0.06676(13) | 0.06676(13) | 0.06676(13) | 0.0522(10) |
| (Ag/In)$_2$     | 0         | 0 | 0.09055(5) | 0.24475(6) | 0.0272(3) |
| (Ag/In)$_3$     | 0.400(5)  | 0.1216(2) | 0.1216(2) | 0.1216(2) | 0.0429(10) |
| (Ag/In)$_4$     | 1         | 0.34769(4) | 0.10822(4) | 0.19736(4) | 0.0220(2) |
| (Ag/In)$_5$     | 1         | 0 | 0 | 0.40971(7) | 0.0298(4) |
| (Ag/In)$_6$     | 1         | 0 | 0.34788(5) | 0.40673(5) | 0.0164(2) |
| (Ag/In)$_7$     | 1         | 0 | 0.5 | 0.30907(7) | 0.0259(4) |
| (Ag/In)$_8$     | 0.369(3)  | 0.27215(15) | 0.27215(15) | 0.27215(15) | 0.0436(7) |
| (Ag/In)$_9$     | 0.600(5)  | 0.33475(11) | 0.33475(11) | 0.33475(11) | 0.0287(5) |
| (Ag/In)$_10$    | 0.092(6)  | 0.0616(12) | 0 | 0.0932(12) | 0.090(9) |

Table 2. Refined atomic parameters for the average substructure of the Eu-(Ag/In) 1/1 approximant.
Table 3. Refined atomic parameters for the structure of the Eu-(Ag/In) 2/1 approximant.

In contrast to previous TEM studies, the single crystal X-ray diffraction experiments on the corresponding 1/1 Eu-Ag-In phase performed as part of this work do not indicate the presence of any superstructure and only the average structure could be refined. The average structure reveals substantial occupancy of the interstitial atomic positions within the cubic cavities which are responsible for the formation of the superstructure in the related Eu₄Cd₂₅ phase, these interstitial atomic positions are denoted Ag-In₈ in table 2. Powder samples containing the 1/1 Eu-Ag-In phase were measured at the SPring-8 synchrotron facility and although weak additional peaks could be seen in the powder patterns, these could not be indexed with the expected supercell. The rather strong intrinsic intensity variations among these additional peaks when compared with other powder samples having somewhat different sample history led to the conclusion that these peaks arise due to unidentified impurities in the samples. The fact that superlattice ordering could be detected by electron diffraction but not by single crystal or synchrotron powder XRD indicates that the 1/1 Eu-Ag-In phase exhibits short to medium range superlattice ordering and that the size of the superlattice domains is too small in relation to the coherence length of the used X-rays, but can obviously be detected by selected area electron diffraction (SAED). The refinement result on the average structure confirm that indeed the phase is a 1/1 approximant of the Yb-Cd family and the observed disorder along the 3-fold axes of the cubic unit cell can be seen as a weighted average atomic decoration between the Eu₄Cd₂₅ superstructure and a standard Yb-Cd type 1/1 approximant. The refined average basic structure is seen in figure 3 a, where the disorder and partially occupied positions along the 3-fold axes is clearly seen.

Single crystals of the 2/1 Eu-Ag-In approximant could be isolated from a multiphase sample and analysed by single crystal X-ray diffraction. The results show that this 2/1 approximant also belongs to the Yb-Cd family of 2/1 approximants, but with a unique degree of structural perfection. Other known 2/1 approximants of this family will display severe positional disorder (in particular the binary phases Yb₁₃Cd₇₆ and Ca₁₃Cd₇₆) or partial occupancies in the atomic positions defining the central tetrahedron of the atomic cluster.[3, 5] It would seem that the introduction of Ag and In instead of Cd allows for the formation of the 2/1 approximant in this system (no 2/1 approximant has been found in the Eu-Cd system) and furthermore, the partial chemical disorder that is introduced in the ternary 2/1 Eu-Ag-In approximant apparently replaces the positional disorder that is usually found in these phases. As a consequence of the perfect order of the tetrahedron in the centre of the cluster, the next atomic shell (the dodecahedron, figure 1 b) is severely distorted as seen in figure 3 b.
Figure 3. In a, the cell-content of the Eu-Ag-In 1/1 approximant is displayed with thermal ellipsoids at the 70% probability level. Eu atoms are seen in red, Ag/In in grey. The disorder along 3-fold axes and in the central tetrahedron is clearly seen. In b, we see the central tetrahedron and surrounding dodecahedron in the cluster of the Eu-Ag-In 2/1 approximant. Atoms are displayed as electron density iso-surfaces at the 8 eÅ⁻³ level, tetrahedron atoms are seen in red. In this phase the tetrahedron has no disorder but the dodecahedral cage is severely distorted.

Chemical and positional disorder are two of the major difficulties encountered when analysing the structures of quasicrystals and approximants. Most quasicrystals are ternary and usually suffer from both chemical and positional disorder. The most efficient way to counter these difficulties is by combined structural studies of both quasicrystals and approximants. Although the same problems are encountered in approximant phases, they can be treated by well established classical methods of structure analysis. In this context the structure of the 2/1 Eu-Ag-In approximant determined as part of this work plays a crucial role: although the partial chemical order between Ag and In has not yet been analysed, this phase is certainly the best choice among ternary 2/1 approximants in the RE-Ag-In systems for such analyses since the structure is essentially devoid of positional disorder. Thus the troublesome correlations between occupational parameters and atomic displacement parameters that are otherwise encountered in the structure refinement can be completely avoided. In order to study the chemical order between Ag and In however, it is necessary to use special techniques such as anomalous X-ray diffraction. Furthermore the well ordered structure of this phase can be used to model and understand the local structures of other positionally disordered 2/1 approximants.

4. Acknowledgements
The authors would like to thank Prof. S. Lidin for valuable discussions and Prof. H. Yamane for his assistance during the single crystal measurements. This work was partially funded by the Japan Science and Technology Agency, Solution Oriented Research for Science and Technology (JST-SORST), and by World Premier International Research Center Initiative (WPI Initiative) on Materials Nanoarchitectonics, MEXT, Japan.

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