Lawrence Berkeley National Laboratory

Recent Work

Title

DETERMINATION OF THE COMPOSITION OF THE ICOSAHEDRAL PHASE IN RAPIDLY SOLIDIFIED Al-Mn QUASICRYSTALS AT HIGH SPATIAL RESOLUTION

Permalink

<https://escholarship.org/uc/item/32j0n694>

Authors

Krishnan, K.M.

Gronsky, R.

Tanner, L.E.

Publication Date

1985-10-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 20 1985

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to Scripta Metallurgica

DETERMINATION OF THE COMPOSITION OF THE
ICOSAHEDRAL PHASE IN RAPIDLY SOLIDIFIED Al-Mn
QUASICRYSTALS AT HIGH SPATIAL RESOLUTION

K.M. Krishnan, R. Gronsky, and L.E. Tanner

October 1985

For Reference

Not to be taken from this room

LBL-20369
c1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

DETERMINATION OF
THE COMPOSITION OF THE ICOSAHEDRAL PHASE
IN RAPIDLY SOLIDIFIED Al-Mn QUASICRYSTALS
AT HIGH SPATIAL RESOLUTION

Kannan M. Krishnan and Ronald Gronsky
National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

and

Lee E. Tanner
Chemistry and Materials Science Department
Lawrence Livermore National Laboratory, P. O. Box 808
Livermore, CA 94550

Abstract

The composition of the quasicrystalline icosahedral phase in rapidly solidified binary Al-Mn alloys has been determined at high spatial resolution by energy dispersive x-ray microanalysis using convergent probes of 200nm diameter. The icosahedral phase is found to have a composition of 20.3 ± 2.0 at%Mn, balance Al, while the metastable aluminum-rich matrix phase contains 4.4 ± 0.4 at%Mn. It is noted that this concentration ratio (4:1) has been known to be important in certain glass forming systems and may have implications in answering the fundamental crystallographic question of the atomic positions occupied by the two elements in the quasicrystal.

The existence of a metallic solid with long-range orientational order and an icosahedral point group inconsistent with lattice translations in rapidly solidified samples of aluminum alloyed with manganese has been recently reported [1,2] based on electron diffraction measurements. The interpretation of these diffraction patterns using a multiple twinning model [3] has been shown to be inconsistent with experimental observations [4,5]. Furthermore, the problem of double diffraction that is crucial to the interpretation of these electron diffraction patterns has been overcome by high-resolution x-ray scattering measurements using a synchrotron source [6], yielding an indexing scheme for peaks in the x-ray diffraction patterns as a sum of icosahedral vectors. Further, the point group of this phase has been conclusively shown to be the icosahedral $m\bar{3}5$ by convergent beam electron diffraction [7].

There are no published theories that satisfactorily explain these experimental observations [8,9]. However, phenomenological models based on Landau theory with the point symmetry of the icosahedron and quasiperiodic or incommensurate translational order have been presented [10-12]. These models accurately reproduce the observed

diffraction patterns, but the position of the most intense peaks scale with τ^{-1} unlike the experiments where they scale with τ^{-3} [8,13]. An alternative approach is to interpret the experimental data as a projection in three dimensions of a six-dimensional regular crystal. Katz and Duneau [14] and independently, V. Elser [15] have computed the diffraction pattern of a three-dimensional Penrose pattern [16] using an elegant projection scheme from a higher dimensional periodic lattice. They find δ -function peaks that are dense in reciprocal space, where the most intense peaks not only account for the peak positions in the Al-Mn diffraction patterns but also scale as τ^{-3} . However, an understanding of the peak intensities is as yet non-existent for this would entail a detailed knowledge of the distribution of the aluminum and manganese atoms in the quasilattice. In order to solve this problem it is necessary to first determine the composition of the icosahedral phase as accurately as possible. This is complicated because the icosahedral phase is formed over a range of starting compositions (10-25 atom-percent manganese) and the microstructure is such that these grains with icosahedral symmetry typically reach an average diameter of only 1-2 microns and they are embedded in an aluminum-rich matrix phase [1]. Preliminary studies suggest [6] an average optimal manganese content of 22 at%. In this report, we present the first detailed results of the determination of the composition of the icosahedral phase by energy dispersive x-ray spectroscopy measurements using convergent electron probes of 200nm diameter.

A sample of starting composition 74.7 wt%Al - 25.3 wt%Mn and a standard of composition 96.5 wt%Al - 3.5 wt%Mn were prepared by arc melting and splat quenching (hammer and anvil) with cooling rates of 10^{6-7} °C/s [17]. Thin foil specimens for electron microscopy were prepared either by jet electropolishing in a nitric acid-methanol electrolyte or by standard ion-milling techniques. Preliminary observations indicated that the first sample was composed of two phases, an icosahedral phase and a face centered cubic aluminum-rich phase, and the standard was a homogeneous single phase alloy. The

composition of the latter sample was determined in both as-melted (bulk) and splat-quenched conditions in a commercial laboratory [18] by atomic absorption spectroscopy to be 3.6 ± 0.18 wt%Mn - 96.4 wt%Al and 3.73 ± 0.19 wt%Mn - 96.27 wt%Al respectively.

Measurements were made on a JEOL 200CX analytical electron microscope at an acceleration voltage of 200kV using a lithium-drifted silicon energy dispersive x-ray detector at a take-off angle of 72° and with a resolution of 155eV for the Mn- k_α (5.9 keV) radiation. A convergent probe of 200nm diameter and a count rate of 1500 cts/sec were employed. Absorption in the specimen could be neglected for this geometry as all measurements were carried out on 20-30nm thick regions of the sample. Typical energy dispersive x-ray spectra from spatially resolved regions of the sample (both the matrix and icosahedral phases) are shown in Fig. 1. Please note that the matrix-phase is not pure aluminum as is generally believed [6] but has a certain fraction of alloyed manganese.

The cross-section for inner shell ionizations (Q) in thin transmission electron microscope foils can be assumed constant through the depth of the film as there are few backscattered electrons and the energy lost by the fast electrons is a negligible fraction of their incident energy. The characteristic x-ray intensity for an element A can then be given by a simplified formula

$$I_A = \text{constant } C_A \omega_A Q_A a_A \epsilon_A / A_A \quad (1)$$

where C is the concentration, ω is the fluorescence yield, a is the relative transition probability ($k_\alpha / (k_\alpha + k_\beta)$) and ϵ is the efficiency of detection of x-rays [19]. Further, the composition ratio (C_A / C_B) of two elements A and B can be related to the characteristic x-ray intensity ratio (I_A / I_B) through the Cliff and Lorimer factors [20] defined as

$$K_{A,B} = \frac{(Q\omega a/A)_B}{(Q\omega a/A)_A} \frac{\epsilon_B}{\epsilon_A} \quad (2)$$

such that

$$\frac{C_A}{C_B} = K_{A,B} \frac{I_A}{I_B} .$$

These K-factors are best determined experimentally using homogeneous standards of known composition because of the uncertainty in the calculated values of Q and the difficulty in determining ϵ [21].

In this study, using the standard specimen of well established composition (Al -3.5 wt%Mn), the factor $K_{Mn,Al}$ was determined to be 0.92 ± 0.04 . The compositions of the icosahedral phase and the aluminum-rich matrix phase under identical experimental conditions were then determined for a large number of samples. Results of this analysis are shown in Table 1.

Table 1

	<u>Icosahedral Phase</u>		
	Intensity (Arbitrary Units)	Weight Percent	Atomic Percent
Aluminum (k_α)	366.61	65.87	79.7 ± 2.0
Manganese (k_α)	199.28	34.13	20.3 ± 2.0
	<u>Matrix Phase</u>		
	Intensity	Weight Percent	Atomic Percent
Aluminum (k_α)	415.6	91.42	95.6 ± 0.4
Manganese (k_α)	40.9	8.58	4.4 ± 0.4

The crystallites were tilted through the three symmetry axes of the icosahedral phase before the characteristic x-ray measurements were made to ensure that they were not any of the related phases identified in the literature [22].

These results have implications in the interpretation of growth models for the quasi-crystalline phase and in answering the fundamental crystallographic question of the atomic positions occupied by the constituent elements. Even though it is recognized that the microstructure obtained by rapid solidification is a two phase mixture, it is generally assumed [6] that the matrix phase is pure aluminum. We have conclusively shown that this is not so, suggesting that the matrix is a metastable phase with limited solid solubility of manganese in aluminum. Further, the composition of the matrix phase should be a function of the cooling rate and since the variation in the composition of the icosahedral phase is small, any compositional changes will have to be accommodated by a change in the volume fraction of the two phases.

The compositional analysis of the icosahedral phase (~80 at%Al, 20 at%Mn) confirms earlier predictions [6]. From the crystallographic point of view, it indicates a concentration ratio of 4:1 for aluminum:manganese atoms. This information must therefore be incorporated in structural models of the quasicrystals including, for example, the packing of the two rhombohedral units that make up the currently accepted 3-D Penrose type models [11,12,14,15].

Significantly, it has been suggested that many metallic glasses contain icosahedral short-range order broken by wedge disclination lines [23]. It is furthermore known that Al-Mn [24] as well as Al-Cr [25] (which also shows an icosahedral phase [1,6]) are glass-formers at higher cooling rates. The glass forming compositions in metal-metalloid systems that are frequently cited [26] exhibit this same composition ratio (80:20), and recently a transformation from such a glassy metal-metalloid alloy of composition $(\text{Pd}_{100-x-y}\text{U}_x\text{Si}_y, x = y = 20 \text{ at}\%)$ to a single phase icosahedral quasi-crystal has been reported [27]. In addition, Chen et al. [28] have drawn critical structural and property comparisons between crystalline Al_6Mn and the Al-Mn icosahedral phase with glassy $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$. This confirms the underlying importance of the composition (80-20) or concentration ratio (1:4) in understanding the structure of these quasicrystals, and points

to possible relationships between certain special topographic and compositional short range order considerations in models of metallic glasses and these icosahedral phases.

Similar compositional analyses have also been carried out in this laboratory on ternary Al-Mn-Si icosahedral quasicrystalline phases. The composition (69.96 at%Al, 7.24 at%Si, 22.80 at%Mn) suggests that the change in the phase field is small and is close to the binary composition within experimental errors. The implications of these accurate stoichiometric studies on a possible structural model and the extent of the metastable phase field are currently being investigated [29].

The authors would like to acknowledge the assistance of Ms. Wendy Smith and Mr. Michael Bryant in specimen preparation, Mr. C. J. Echer in the operation of the 200CX AEM, Mr. M. Wall in preliminary TEM examination and Mr. R. Castro in alloy and rapid solidification fabrication. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, U. S. Department of Energy under Contract Nos. DE-AC03-76SF00098 and W-7405-Eng-48.

References

1. D. Shechtman and I. A. Blech, Met. Trans. 16A, 1005 (1985).
2. D. Shechtman, I. A. Blech, D. Gratias and J. W. Cahn, Phys. Rev. Lett. 53, 1951 (1985).
3. R. D. Field and H. L. Frazer, Mat. Sci. Eng. 68, L17 (1984-85).
4. R. Gronsky, K. M. Krishnan and L. E. Tanner, Proc. 43rd Annual EMSA Meeting, Louisville, Kentucky, p. 34 (1985).
5. D. Shechtman, D. Gratias and J. W. Cahn, C. R. Acad. Sci. Paris 18, 909 (1985).
6. P. A. Bancel, P. A. Heiney, P. W. Stephens, A. I. Goldman and P. M. Horn, Phys. Rev. Lett. 54, 2422 (1985).
7. L. A. Bendersky and M. J. Kaufman, submitted to Phil. Mag. Lett. (1985).
8. D. R. Nelson and B. I. Halperin, Science 229, 233 (1985).
9. A. L. Mackay and P. Kramer, Nature 316, 17 (1985).
10. P. Bak, Phys. Rev. Lett. 54, 1517 (1985).
11. D. Levine, T. C. Lubensky, S. Ostlund, S. Ramaswamy, P. J. Steinhardt and J. Toner, Phys. Rev. Lett. 54, 1520 (1985).
12. N. D. Mermin and S. M. Troian, Phys. Rev. Lett. 54, 1524 (1985).
13. τ is the golden mean and is defined as $\tau = (\sqrt{5}+1)/2$.
14. M. Duneau and A. Katz, Phys. Rev. Lett. 54, 2688 (1985).
15. V. Elser, AT and T Bell Labs. preprint.
16. A non-periodic tessellation of space by rhombohedra of two kinds.
17. L. E. Tanner and R. Ray, Acta Met. 27, 1727 (1979).
18. Anamet Laboratories, Inc., Berkeley, California 94710.
19. Introduction to AEM, (eds. J. J. Hren, J. I. Goldstein and D. C. Joy), Plenum Press, N.Y. (1979), p. 83.

20. G. Cliff and G. W. Lorimer, J. Microscopy 103, 203 (1975).
21. D. B. Williams, D. E. Newbury, J. I. Goldstein and C. E. Fiori, J. Microscopy 136, 209 (1984).
22. L. Bendersky, R. J. Schaeffer, F. S. Biancaniello, W. J. Boeinger, M. J. Kaufman and D. Shechtman, Scripta Met. 19, 909 (1985).
23. D. R. Nelson, Phys. Rev. B28, 5515 (1983).
24. D. Shechtman as cited in Ref. [8].
25. P. Furrer and H. Warlimont, Mat. Sci. Eng. 28, 127 (1977).
26. H. S. Chen, H. J. Leamy and C. E. Miller, Ann. Rev. Mater. Sci. 10, 363 (1980).
27. S. J. Poon, A. J. Dremen and K. R. Lawless, submitted to Phys. Rev. Lett. (1985).
28. H. S. Chen, C. H. Chen, A. Inoue and J. T. Krause, Phys. Rev. B32, 1940 (1985).
29. R. Gronsky, K. M. Krishnan and L. E. Tanner, to be published.

Fig. 1. Typical energy dispersive x-ray spectra from the matrix phase (a) and the icosahedral phase (b) are shown. A counting time of 300 seconds and a count-rate of 1500 cts/s were used to ensure good statistics.

Fig. 1

XBL 858-3536

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*