

Structural and Mossbauer effect studies of quasicrystalline Al-Pd-Cr-Fe alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 663

(<http://iopscience.iop.org/0953-8984/5/6/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 01:06

Please note that [terms and conditions apply](#).

Structural and Mössbauer effect studies of quasicrystalline Al–Pd–Cr–Fe alloys

Z Wang, R A Dunlap and D W Lawther

Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

Received 14 September 1992

Abstract. Structural studies of conventionally solidified $\text{Al}_{80-2x}\text{Pd}_{20}\text{Cr}_x\text{Fe}_x$ alloys have shown that the formation of a well ordered icosahedral phase occurs for a composition where the free-electron Fermi sphere is coincident with the first pseudo-Brillouin zone boundary. This condition indicates the importance of the Hume-Rothery stabilization criterion for icosahedral phase formation in this system. Mössbauer effect studies show the similarity of the local structural order in stable $\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$ to that found in stable quasicrystalline Al–Cu–Fe alloys and indicate a higher degree of structural order compared with that found in metastable icosahedral alloys prepared by non-equilibrium processing techniques.

1. Introduction

The discovery of stable phases which exhibit quasicrystalline order has been an important advancement in the understanding of the microstructure of these unique materials. Recent work by Tsai *et al* (e.g. [1]) on the application of Hume-Rothery stabilization criteria to quasicrystalline alloys has helped to clarify the fundamental physical principles responsible for the formation of these phases.

The Mössbauer effect has been an important technique for the study of the quasicrystalline phase. The occurrence of Fe in many metastable quasicrystalline alloys and its ability to substitute for other transition metals in many others has been responsible for the widespread use of the Mössbauer effect technique for the study of this class of materials (see, e.g. [2]). The use of this technique for the study of stable quasicrystals has been limited to two different systems: icosahedral Al–Cu–Fe (see, e.g. [3]) and decagonal Al–Pd–Fe [4]. Difficulty in understanding the Mössbauer results for the Al–Cu–Fe system arises from the complexity of the phase diagram of these alloys as a function of composition and heat treatment and the similarity of the x-ray and electron diffraction results for quasicrystalline and approximant crystalline phases [3, 5–8].

The recent discovery of a well ordered quasicrystalline phase in the Al–Pd–Mn system [9, 10] has provided the opportunity for studying the physical properties of stable icosahedral quasicrystals in a system which is much less sensitive to variations of stoichiometry and thermal treatment than the Al–Cu–Fe system. The further discovery by Tsai *et al* [11] that the stable icosahedral phase in this system may be retained when Mn is replaced by a combination of Cr and Fe has provided a system in which Mössbauer effect studies may be undertaken for comparison with previous studies of Al–Cu–Fe alloys.

In the present work we report a study of the formation of the stable icosahedral phase in the $\text{Al}_{80-2x}\text{Pd}_{20}\text{Cr}_x\text{Fe}_x$ system prepared by equilibrium processing techniques. The relationship of the region of icosahedral phase formation to the stability criteria predicted by Hume-Rothery [12] is discussed. Results of ^{57}Fe Mössbauer effect spectroscopy studies of the stable icosahedral phase are presented and these are discussed in terms of previous Mössbauer effect studies of stable and metastable quasicrystalline alloys.

2. Sample preparation and experimental techniques

Alloys of the composition $\text{Al}_{80-2x}\text{Pd}_{20}\text{Cr}_x\text{Fe}_x$ with $x = 3, 4, 5$ and 6 have been prepared by melting high-purity elemental components in an argon arc furnace. Ingots were ground and annealed under argon for a period of 24 h at 900°C followed by quenching in ice-water. Room temperature $\text{Cu K}\alpha$ x-ray diffraction patterns were obtained using a Siemens D500 scanning diffractometer. Room temperature ^{57}Fe Mössbauer effect spectra were obtained using an Austin S-600 constant acceleration spectrometer and a Pd^{57}Co source. The intrinsic spectrometer linewidth was 0.24 mm s^{-1} for a thin $\alpha\text{-Fe}$ absorber.

3. Results

Typical x-ray diffraction patterns for the series of alloys studied here are shown in figure 1. The alloy with $x = 4$ shows an essentially single-phase icosahedral quasicrystal structure while all other alloys prepared here show the presence of a measurable quantity of impurity phase.

A typical room temperature Mössbauer effect spectrum for the icosahedral alloys studied here, i.e. for $\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$, is illustrated in figure 2. This spectrum consists of a well defined quadrupole split doublet with a substantial degree of asymmetry. Mössbauer effect spectra of the other alloys studied in this work also showed the presence of a quadrupole split doublet although for the $x = 5$ alloy structure was observed in the shape of the absorption lines. This is presumably due to the presence of Fe in the impurity phase which exists in this alloy. As impurity lines are present in the x-ray diffraction patterns of all alloys except $\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$, a detailed investigation was only made of the Mössbauer spectrum of the single-phase composition.

Although the suitability of various fitting methods for the analysis of ^{57}Fe Mössbauer effect spectra of quasicrystalline materials has been discussed at length by several authors (see, e.g., [2]), a definitive interpretation of the results in absolute terms is not generally accepted. It is, however, useful to compare fitted Mössbauer parameters for different quasicrystalline materials and it has been established that systematic trends in these parameters can be reliably related to variations in the local order present in the alloys [13]. For the purpose of comparing the present results to those previously reported for other icosahedral quasicrystals, we have analysed the spectrum shown in figure 2 on the basis of the shell model [14, 15]. This expands the quadrupole splitting distribution, $P(\Delta)$, as

$$P(\Delta) \propto (\Delta/\sigma)^n \exp(-\Delta^2/2\sigma^2) \quad (1)$$

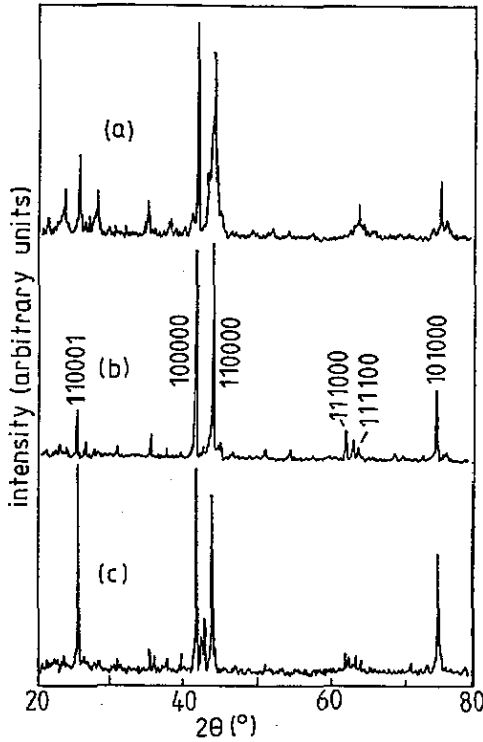


Figure 1. Typical room temperature x-ray diffraction patterns of $Al_{80-2x}Pd_{20}Cr_xFe_x$ for (a) $x = 3$, (b) $x = 4$ and (c) $x = 5$, obtained using $Cu K_{\alpha}$ radiation. Icosahedral indices are shown for the $x = 4$ pattern.

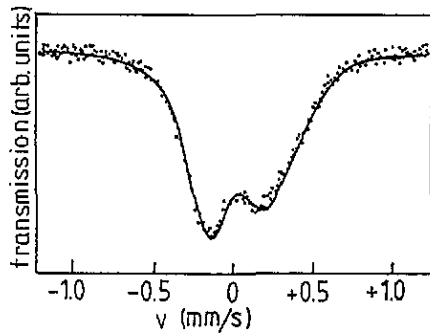


Figure 2. Room temperature ^{57}Fe Mössbauer effect spectrum of icosahedral $Al_{72}Pd_{20}Cr_4Fe_4$. The solid line is a fit to the shell model as described in the text.

where n and σ are fitted parameters. In order to account for the spectral asymmetry we have expressed the correlation between the isomer shift, δ , and the quadrupole splitting as

$$\delta(\Delta) = \delta_0 + \alpha\Delta \tag{2}$$

where δ_0 and α are fitted parameters. The resulting quadrupole distribution obtained from this analysis is illustrated in figure 3 and the fitted parameters n and α are given in table 1. The table also gives values of the mean isomer shift, the mean quadrupole splitting and the width of the quadrupole distribution as defined by Lawther *et al* [16].

4. Discussion

The stability of the quasicrystalline phase has been discussed by Tsai *et al* [1] on the basis of mechanisms described by Hume-Rothery [12]. This stabilization condition requires that the diameter of the free electron Fermi sphere is equal to the diameter of the first pseudo-Brillouin or Jones zone boundary, K_P , i.e.

$$2k_F = K_P \tag{3}$$

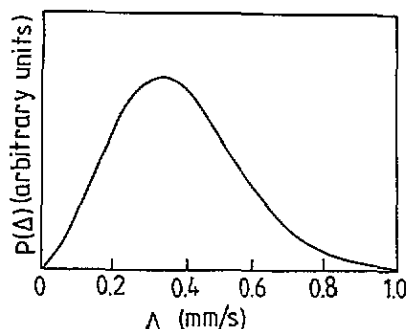


Figure 3. Shell distribution of quadrupole splittings, $P(\Delta)$, for icosahedral $\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$ as described in the text.

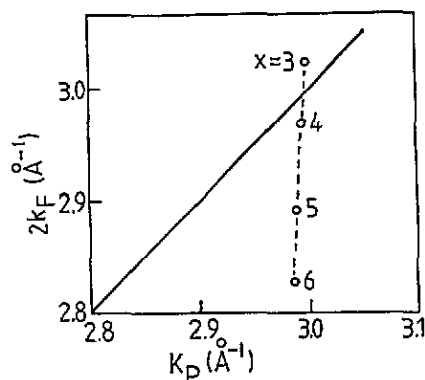


Figure 4. Plot of $2k_F$ versus K_P for the $\text{Al}_{80-2x}\text{Pd}_{20}\text{Cr}_x\text{Fe}_x$ alloys studied here as given by the data in table 2. The solid line represents the stability condition given by $2k_F = K_P$. Values of x , indicating the composition, are shown for each data point.

Table 1. Comparison of Mössbauer effect parameters for the stable icosahedral alloys Al-Pd-Cr-Fe and Al-Cu-Fe and the metastable icosahedral alloys Al-Fe-Mo and Al-Fe-Ta. The Al-Cu-Fe sample was prepared by arc melting followed by annealing at 1073 K for 24 h and quenching in ice-water. Al-Cu-Fe data are from reference [3]. The Al-Fe-Mo and Al-Fe-Ta samples were prepared by rapid solidification from the melt and these data are from references [16, 22].

Alloy	n	α	$\bar{\delta}$ (mm s^{-1})	$\bar{\Delta}$ (mm s^{-1})	$\langle \Delta \rangle$ (mm s^{-1})	$\langle \Delta \rangle / \bar{\Delta}$
$\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$	1.64	+0.12	+0.154	0.376	0.427	1.14
$\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$	1.57	+0.005	+0.234	0.379	0.438	1.16
$\text{Al}_{80}\text{Fe}_{11}\text{Mo}_9$	1.48	+0.002	+0.275	0.444	0.579	1.30
$\text{Al}_{70}\text{Fe}_{20}\text{Ta}_{10}$	1.14	-0.051	+0.216	0.410	0.585	1.43

where k_F is the Fermi wave vector. In both icosahedral and decagonal quasicrystals this condition has been shown to be met [1, 17, 18] for a value of the average electron density per atom of $e/a \simeq 1.75$.

The validity of this stability condition for the present alloys may be considered on the basis of values of K_P as determined from x-ray diffraction studies and values of $2k_F$ as determined on the basis of electron density calculations. The pseudo-Brillouin zone diameter is obtained from the positions of the most intense x-ray diffraction peaks as

$$K_P = (4\pi/\lambda) \sin(\theta) \quad (4)$$

where θ is the scattering angle. In the present work on icosahedral structures K_P was taken to be the mean value for the (100 000) and (110 000) reflections weighted by their relative intensities. These results are given in table 2.

The free electron Fermi wave vector is determined from

$$k_F = \sqrt{(3\pi^2 n_0)} \quad (5)$$

Table 2. Calculated electronic properties of $\text{Al}_{80-2x}\text{Pd}_{20}\text{Cr}_x\text{Fe}_x$ and measured inverse scattering lengths as described in the text.

x	e/a	ρ (g cm^{-3})	n_0 (\AA^{-3})	$2k_F$ (\AA^{-1})	K_P (\AA^{-1})
3	1.87	4.61	0.1171	3.027	3.005
4	1.74	4.71	0.1191	2.964	2.996
5	1.61	4.81	0.1024	2.895	2.998
6	1.48	4.91	0.0948	2.821	2.983

where n_0 is the electron density. Dunlap [19] has expressed the electron density in terms of the average conduction electron contribution per atom, e/a , to be

$$n_0 = (e/a)\rho N_A / \langle A \rangle \quad (6)$$

where ρ is the alloy density, N_A is Avogadro's number and $\langle A \rangle$ is the mean elemental atomic weight of the alloy constituents. The quasicrystal density can be taken to be [19]

$$\rho = \langle \rho \rangle P / \langle P \rangle \quad (7)$$

where $\langle \rho \rangle$ is the mean elemental density, P is the quasicrystal packing fraction and $\langle P \rangle$ is the mean elemental packing fraction. Here we have taken e/a to be the mean elemental valence as given by Raynor [20] and $\langle \rho \rangle$ to be 0.7 as estimated by Werkman *et al* [21]. Results of calculations of values of electronic quantities for the alloys studied in this work are given in table 2. The relationship of the calculated $2k_F$ values and the measured K_P values is illustrated in figure 4. The broken $2k_F$ versus K_P line is seen to cross the solid $2k_F = K_P$ line for a value of x between 3 and 4. This crossing point corresponds to a value of $e/a = 1.79$ and is consistent with our x-ray diffraction studies which indicate that alloys with $x > 4$ show an increasing concentration of non-quasicrystalline impurity phase. The behaviour illustrated in this figure suggests the validity of the Hume-Rothery stabilization mechanism as the relevant fundamental physical phenomenon responsible for the formation of the icosahedral phase in Al-Pd-Cr-Fe alloys.

The ^{57}Fe Mössbauer effect results obtained in this work for the icosahedral $\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$ alloy are compared with previous literature values of the parameters from a shell model fit to spectra of other icosahedral phases in table 1. The following conclusions may be drawn on the basis of the present results.

(i) The value of n is comparable to that found in other stable quasicrystals and is higher than that typically observed in metastable quasicrystalline phases.

(ii) The greater degree of local order which is characteristic of stable, rather than metastable, quasicrystalline alloys is indicated by a smaller relative width of the quadrupole distribution, $\langle \Delta \rangle / \Delta$, as given in table 1.

(iii) The isomer shift in $\text{Al}_{72}\text{Pd}_{20}\text{Cr}_4\text{Fe}_4$ is measurably less positive than that observed in most other Al-based quasicrystals with similar Al content. While the stability studies discussed above indicate very nearly the same average electron density in all Al-based quasicrystalline alloys, the Mössbauer effect studies indicate a measurable difference in the electron density at the Fe nuclear probe site.

A consideration of Mössbauer effect results of Al-Pd-Cr-Fe alloys of other compositions provides some insight into the mechanism for icosahedral phase

formation in this system. While the complex Mössbauer effect spectra of those alloys which show impurity phases are not straightforward to analyse, there is no evidence on the basis of the present investigation that there are measurable differences in the isomer shift of the icosahedral component as a function of alloy composition. This suggests that in alloys with starting compositions other than the ideal icosahedral stoichiometry there is a tendency for the elemental composition of the quasicrystalline phase to remain relatively constant at the expense of the formation of impurity phases.

In summary the present structural studies confirm the applicability of the Hume-Rothery mechanism to the formation of a stable icosahedral quasicrystalline phase in the Al-Pd-Cr-Fe system. Mössbauer effect studies show the similarities of local structural order in icosahedral Al-Pd-Cr-Fe and in the stable quasicrystalline phase of Al-Cu-Fe. However, substantial differences in the isomer shift values indicate significant differences in the local electronic environment of the Fe probe atoms.

Acknowledgments

This work was funded by a grant from the Natural Sciences and Engineering Research Council of Canada.

References

- [1] Tsai A P, Inoue A and Masumoto T 1991 *Sci. Rep. RITU A* **36** 99
- [2] Dunlap R A and Lawther D W 1992 *Mater. Sci. Rep.* submitted
- [3] Lawther D W and Dunlap R A 1992 *J. Non-Cryst. Solids* at press
- [4] Lawther D W and Dunlap R A 1992 *J. Non-Cryst. Solids* at press
- [5] Dunlap R A, Lawther D W and Srinivas V 1992 *Proc. Int. Symp. on the Physics and Chemistry of Finite Systems* ed P Jena, S N Khanna and B K Rao (Dordrecht: Kluwer) p 527
- [6] Bessière M, Quivy A, Lefebvre S, Devaud-Rzepski J and Calvayrac Y 1991 *J. Physique* **1** 1823
- [7] Klein T, Berger C, Mayou D and Cyrot-Lackmann F 1991 *Phys. Rev. Lett.* **66** 2907
- [8] Audier M, Bréchet Y, DeBoissieu M, Guyot P, Janot C and Dubois J M 1991 *Phil. Mag. B* **63** 1375
- [9] Tsai A P, Inoue A, Yokoyama Y and Masumoto T 1990 *Mater. Trans. JIM* **31** 98
- [10] Tsai A P, Inoue A and Masumoto T 1990 *Phil. Mag. Lett.* **62** 95
- [11] Tsai A P, Yokoyama Y, Inoue A and Masumoto T 1992 *Proc. Int. Symp. on the Physics and Chemistry of Finite Systems* ed P Jena, S N Khanna and B K Rao (Dordrecht: Kluwer) p 177
- [12] Hume-Rothery W 1926 *J. Inst. Met.* **35** 295
- [13] Dunlap R A, O'Handley R C, McHenry M E and Srinivas V 1991 *Struct. Chem.* **2** 501
- [14] Czjzek G 1982 *Phys. Rev. B* **25** 4908
- [15] Eibschutz M, Chen H S and Hauser J J 1986 *Phys. Rev. Lett.* **56** 169
- [16] Lawther D W, Dunlap R A, Srinivas V, Lloyd D J and Jha S 1990 *Hyperfine Interact.* **60** 785
- [17] Friedel J and Denoyer F 1987 *C.R. Acad. Sci., Paris* **305** 1365
- [18] Bancel P A and Heiney P A 1986 *Phys. Rev. B* **33** 7922
- [19] Dunlap R A 1992 *Phil. Mag. B* at press
- [20] Raynor G V 1949 *Prog. Met. Phys.* **1** 1
- [21] Werkman R D, Schurer P J, Vincze I and van der Woude F 1989 *Hyperfine Interact.* **45** 409
- [22] Srinivas V and Dunlap R A 1989 *Phys. Rev. B* **40** 9590