Nuclear magnetic resonance study of the Al-Pd-Mn quasicrystalline alloys

1992 J. Phys.: Condens. Matter 4 3043

(http://iopscience.iop.org/0953-8984/4/11/027)

J. Phys.: Condens. Matter 4 (1992) 3043–3050. Printed in the UK

Nuclear magnetic resonance study of the Al–Pd–Mn quasicrystalline alloys

T Shinohara, A P Tsai and T Masumoto
Institute for Materials Research, Tohoku University Sendai 980, Japan

Received 3 September 1991, in final form 5 November 1991

Abstract. The ^{27}Al and ^{55}Mn spin-echo spectra in the Al–Pd–Mn quasicrystalline alloys have been measured as a function of Al content and temperature. The lineshape and peak shift between the simple icosahedral phase and the face-centred icosahedral phase exhibit different characteristics in the ^{27}Al and ^{55}Mn spectra. They are temperature independent in the former phase and markedly temperature dependent in the latter phase. The ^{27}Al Knight shift is almost zero in the $Al_{90-x}Pd_xMn_{10}$-containing simple icosahedral phase with Pd contents x of 5, 10 and 15 whereas that in the $Al_{70}Pd_{20}Mn_{10}$ is negative, suggesting that these phases are in different electronic states.

1. Introduction

There has been intense experimental and theoretical interest in icosahedral-phase (i-phase) quasicrystals since their discovery in 1984 (Shechtman *et al* 1984). Besides the bulk of the literature focused on Al–Mn and Al–Mn–Si alloys, great efforts have been devoted to finding the alloy composition at which the i-phase is formed in metastable and stable states, in addition to the clarification of fundamental properties of the new phase. As a result, many stable icosahedral and decagonal quasicrystals have been found in Al-based alloy systems (Sainfort *et al* 1985, Tsai *et al* 1987, 1988, He *et al* 1988a,b). However, the atomic sites in the quasicrystalline structure have not been definitely determined yet.

On the other hand, the electronic and magnetic properties of quasicrystalline alloys are sensitive to alloy concentration and environmental factors such as coordination number and the interatomic distance. A local probe such as nuclear magnetic resonance (NMR), Mössbauer spectroscopy and extended x-ray absorption fine structure (EXAFS) provide information complementary to x-ray diffraction studies, which can be more effective guides to structural modelling. There have been several NMR studies on the i-phase and related crystalline phase in Al–Mn-based alloys (Warren *et al* 1985, 1986, Rubinstein *et al* 1986, Yasuoka *et al* 1986). The linewidths in the i-phase are much greater than in the crystalline phases. It is now definitely established in the Al–Mn-based alloys that two separate classes of Mn sites exist in the i-phase Al–Mn–Si quasicrystals (Edagawa *et al* 1987, Eibschutz *et al* 1987, 1988).

More recently, Tsai *et al* (1990a,b,c) found that a new and single stable quasicrystalline i-phase in the Al–Pd–Mn alloy exhibits a six-dimensional face-centred icosahedral (FCI) lattice which is better ordered than previously studied simple icosahedral (SI) alloys. The replacement of Pd with Al drastically increases the linewidth

0953-8984/92/113043+08$04.50

of x-ray diffraction by an order of magnitude and the FCI structure transforms to the SI structure (Tsai *et al* 1991).

We here present the first NMR measurement of ^{27}Al and ^{55}Mn in the SI and FCI phases of Al–Pd–Mn system alloys. In particular, we find different temperature dependences of the NMR spectra for these phases, indicating that the magnetic Mn atoms exist only in the FCI phase.

2. Experimental procedure

Ternary alloys of $Al_{90-x}Pd_xMn_{10}$ ($x = 5$, 10, 15 and 20) were melted in an argon atmosphere using an arc furnace. Rapidly solidified ribbon samples were prepared using a single-roller melt-spinning apparatus. All samples were carefully powdered for x-ray diffraction and NMR measurements. The quasicrystalline nature of the as-quenched alloys was examined by x-ray diffraction and transmission electron microscopy. Figure 1 shows x-ray powder diffraction patterns of rapidly solidified Al–Pd–Mn alloys. Indexing of the peak could be made using Elser's (1985) indices. In $Al_{80}Pd_{10}Mn_{10}$ and $Al_{85}Pd_5Mn_{10}$, a certain amount of metallic Al coexisted in the i-phase and no superlattice peak is observed. The superlattice peaks of $\frac{1}{2}(311111)$ and other lines are more intensive and sharp in the $Al_{70}Pd_{20}Mn_{10}$ than in $Al_{75}Pd_{15}Mn_{10}$. The former is a fully single FCI phase with a highly ordered and phasonless structure which has been identified by x-ray and covergent-beam electron diffraction studies (Tanaka 1991, Tsai *et al* 1991). However, for the $Al_{75}Pd_{15}Mn_{10}$ alloy, it is considered that the FCI phase and the SI phase coexist.

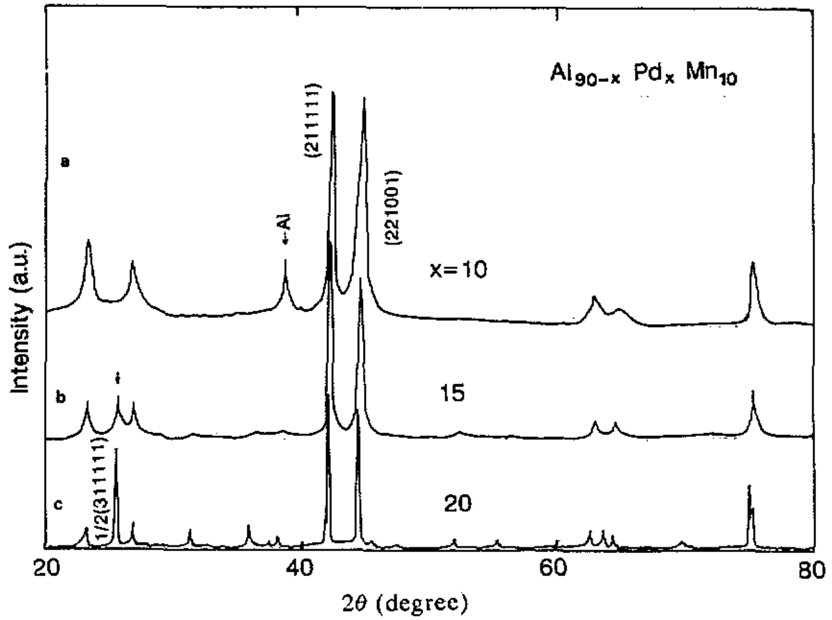

Figure 1. X-ray diffraction patterns for rapidly solidified $Al_{80}Pd_{10}Mn_{10}$ (curve (a)), $Al_{75}Pd_{15}Mn_{10}$ (curve (b)) and $Al_{70}Pd_{20}Mn_{10}$ (curve (c)) alloys.

For the observation of NMR signals, a phase-coherent pulsed NMR spectrometer was utilized. Resonance spectra were obtained by plotting the spin-echo amplitude with a box-car integrator as a function of the external magnetic field. The external magnetic field was swept in two different ranges: a wide-range sweep was performed by changing the current through the coils of a superconducting magnet, while a narrow-range sweep was carried out by changing the current through modulation coils at a fixed magnetic field.

3. Experimental results

Figure 2 shows the ^{27}Al and ^{55}Mn resonance spectra examined at 32.500 Mhz while sweeping the magnetic field in the wide range with changing temperature. A general feature of the ^{27}Al spectra is the relatively narrow central peak associated with the ^{27}Al $m = \pm\frac{1}{2}$ transition superimposed on a broad spectrum due to electric quadrupole splitting. In the FCI phase of $Al_{70}Pd_{20}Mn_{10}$, marked broadening of the central component with decreasing temperature is observed while in the quasicrystal with other Al concentrations the ratio of the intensity of the narrow component to that of the broad component does not exhibit any appreciable change with temperature within experimental error.

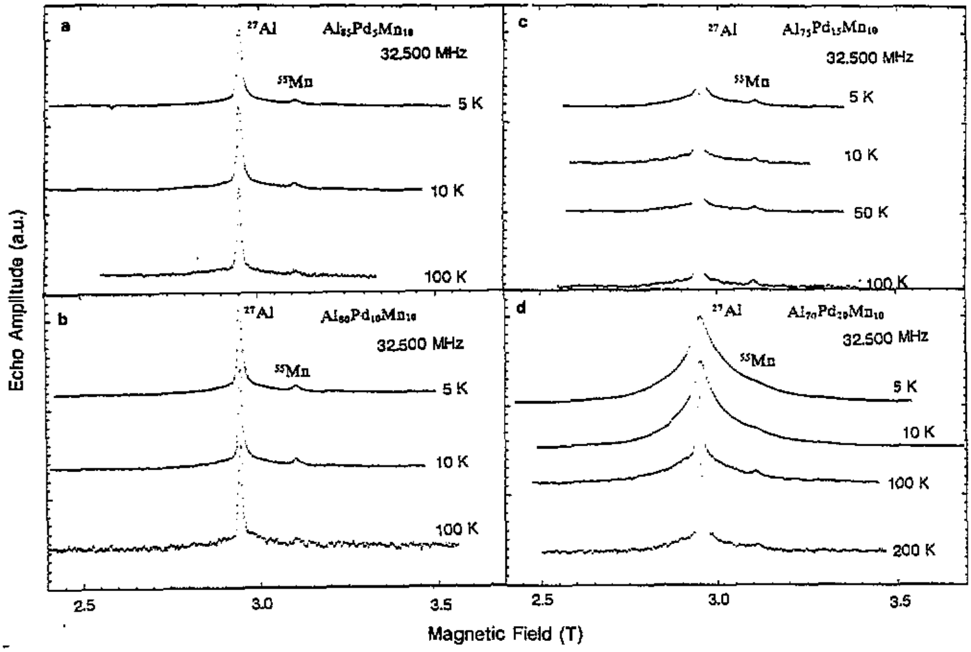

Figure 2. ^{27}Al and ^{55}Mn spin-echo spectra observed at 32.500 MHz as a function of temperature for as-quenched (a) $Al_{85}Pd_5Mn_{10}$, (b) $Al_{70}Pd_{10}Mn_{10}$, (c) $Al_{75}Pd_{15}Mn_{10}$ and (d) $Al_{70}Pd_{20}Mn_{10}$ alloys.

Figure 3 shows the ^{27}Al spectra obtained at a fixed frequency while sweeping the magnetic field in the narrow range. The $(\frac{1}{2})\pi$ pulse length and $(\frac{1}{2})\pi$–π pulse separation were 10 μs and 100 μs respectively. The width of window pulse used for the box-car integrator was 15 μs. For the $Al_{85}Pd_5Mn_{10}$ and $Al_{80}Pd_{10}Mn_{10}$ alloys, it is expected that the spectra in figures 3(*a*) and 3(*b*) are composites of a line from

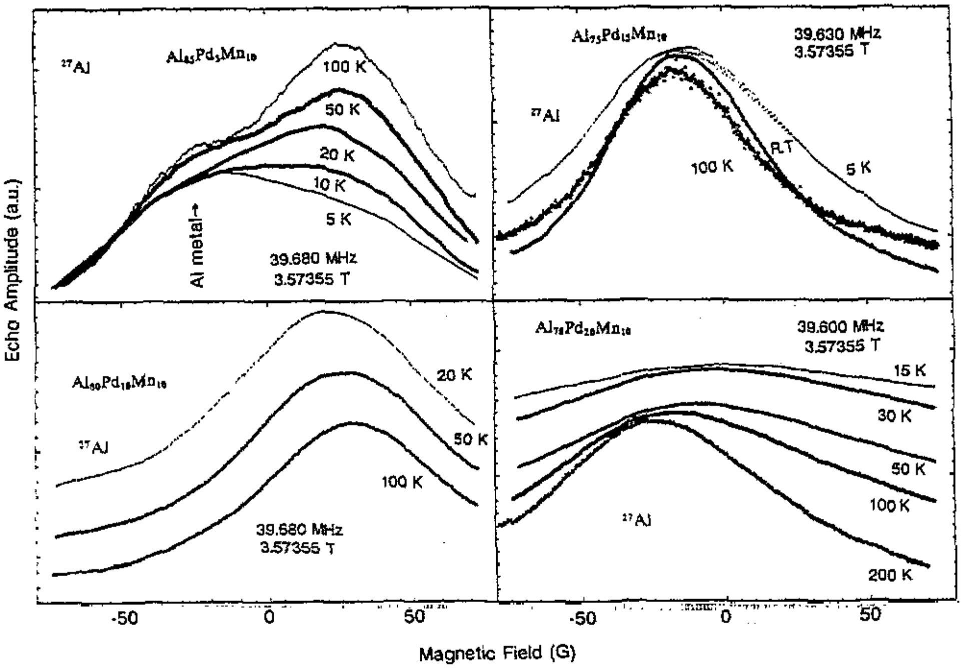

Figure 3. Temperature dependence of ^{27}Al spin-echo spectra obtained at a fixed frequency (denoted in the figure) while sweeping the magnetic field in the narrow range. The magnetic field obtained from the superconducting magnet is 3.57355 T.

metallic Al and the quasicrystal phase and the relative magnitude of these varies with temperature owing to the different temperature dependences of the spin–spin relaxation time. Figure 3(*c*) for Al$_{75}$Pd$_{15}$Mn$_{10}$ indicates that the peak shift (referred to as the Knight shift) of the ^{27}Al spectra is temperature independent and that the widths of the peaks exhibit little change at low temperatures. On the other hand, the Knight shift and the width of the Al spectrum in the FCI phase of the Al$_{70}$Pd$_{20}$Mn$_{10}$ quasicrystal revealed a marked temperature dependence.

Table 1. Knight shift at 5 K.

	Knight shift (%)	
Substance	Al shift	Mn shift
Al$_{70}$Pd$_{20}$Mn$_{10}$	−0.134±0.04[a]	0.20±0.02[c]
Al$_{75}$Pd$_{15}$Mn$_{10}$	0.01±0.02	0.41±0.02
Al$_{80}$Pd$_{10}$Mn$_{10}$	0.028±0.014[b]	0.45±0.02
Al$_{85}$Pd$_5$Mn$_{10}$	−0.01±0.014	0.45±0.02

[a] At 10 K.
[b] The phase containing metallic Al at 20 K.
[c] At 50 K.

The temperature dependence of the ^{55}Mn spin-echo spectra at different temperatures at a fixed frequency while sweeping the magnetic field in the narrow range is shown in figure 4. These behave in a similar way to the above ^{27}Al spin-echo spectra; the Knight shift and the width of the ^{55}Mn spectra for quasicrystal with Al contents of

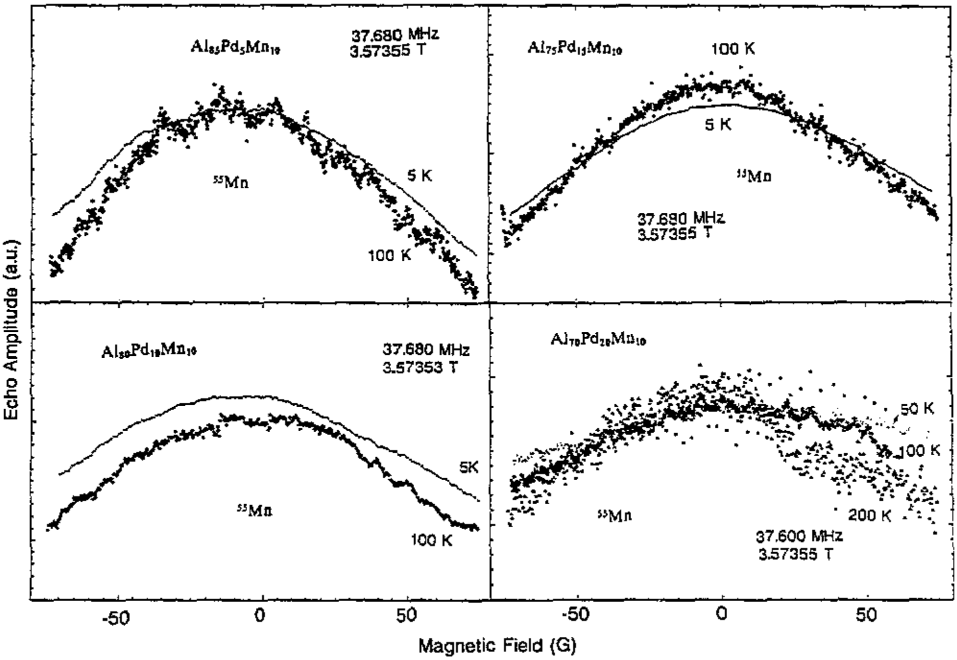

Figure 4. Temperature dependence of ^{55}Mn spin-echo spectra obtained at a fixed frequency while sweeping the magnetic field in the narrow range.

85, 80 and 75 at.% do not seem to vary with temperature whereas for $Al_{70}Pd_{20}Mn_{10}$ quasicrystals the width only changes subtly, even though data could not be obtained below 50 K.

4. Discussion

Although a clear structure cannot be seen in the ^{27}Al spectra in figure 2(*a*) for the $Al_{85}Pd_5Mn_{10}$ quasicrystal, the resonance from metallic Al appears in ^{27}Al spectra when sweeping the magnetic field in a narrow range.

For $Al_{85}Pd_5Mn_{10}$, measurements carried out under different pulse conditions show the resonance from ^{27}Al in the quasicrystal phase (figure 5). The ^{27}Al Knight shift from the SI phase of the quasicrystal remains unchanged with temperature, suggesting that the phase is Pauli paramagnetic. Since metallic Al is also mixed in the SI phase of the $Al_{80}Pd_{10}Mn_{10}$ quasicrystal, the change in the ^{27}Al Knight shift as seen in figure 3(*b*) is also expected to be a composite of a line from metallic Al and the quasicrystal phase. The temperature-independent width except at the lowest temperatures and the Knight shift for the $Al_{75}Pd_{15}Mn_{10}$ quasicrystal are in agreement with the data from magnetic susceptibility measurements which indicates the phase to be Pauli paramagnetic (Fukamichi *et al* 1991a,b). For the $Al_{70}Pd_{20}Mn_{10}$ quasicrystal, even though the change in the ^{27}Al Knight shift with temperature is firstly indicated, broadening of the width of the ^{27}Al and ^{55}Mn spectra on decrease in the temperature is compared with the well known result observed in Al–Mn and Al–Mn–Si quasicrystals in which the width of the ^{27}Al spectra becomes broader at low temperatures (Warren *et al* 1986, Yasuoka *et al* 1986). It is suggested that magnetic

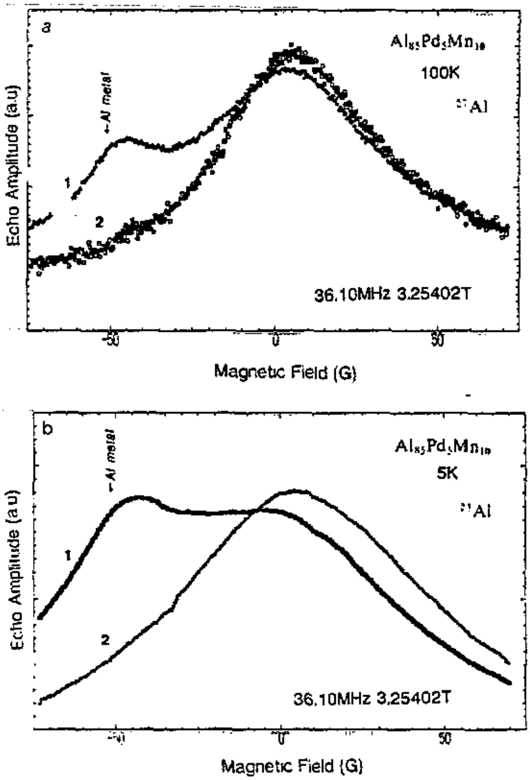

Figure 5. ^{27}Al spin-echo spectra measured under different pulse separations at 36.10 MHz for a magnetic field of 3.254 02 T from the superconducting magnet at (a) 100 K and (b) 5 K: spectrum 1, obtained in 40 μs of the $\frac{1}{2}\pi$ pulse length and 170 μs of pulsed separation; spectrum 2, obtained with the same pulse length and 500 μs pulse separation.

Mn atoms exist in the FCI phase of $Al_{70}Pd_{20}Mn_{10}$ quasicrystals, consistent with the bulk magnetic susceptibility (0.4 μ_B per Mn atom) (Fukamichi *et al* 1991a,b). The resonance signal from the magnetic Mn atom could not be seen in the above spectra because of rapid spin–spin relaxation time and/or broadening. Figure 6 shows the ^{27}Al and ^{55}Mn Knight shifts as a function of temperature and these values at 5 K are summarized in table 1. The difference between the ^{27}Al and ^{55}Mn Knight shifts for $Al_{70}Pd_{20}Mn_{10}$ is very different from those for alloys, the other indicating that these phases in the quasicrystal are in a different electronic state. The fact that the ^{27}Al Knight shift in the quasicrystal with Al contents of 85, 80 and 75 at.% is almost zero suggests that the Al atoms donate most s and p electrons to the 3d band in Mn atoms, resulting in the disappearance of the magnetic moment. The temperature-independent ^{55}Mn Knight shift in these quasicrystals indicates that the 3d and 4d bands are Pauli paramagnetic. In contrast, for the $Al_{70}Pd_{20}Mn_{10}$ quasicrystal, it is considered that there is a hole in the d band, following the appearance of the magnetic Mn atom. The behaviour of the ^{27}Al Knight shift in the $Al_{70}Pd_{20}Mn_{10}$ quasicrystal suggests that conduction electron polarization caused by magnetic Mn atoms may induce a negative and temperature-dependent Knight shift at the Al atom. The smaller ^{55}Mn Knight shift observed in the $Al_{70}Pd_{20}Mn_{10}$ quasicrystal may also be due to such polarization from Mn atoms. The difference between the ^{55}Mn Knight

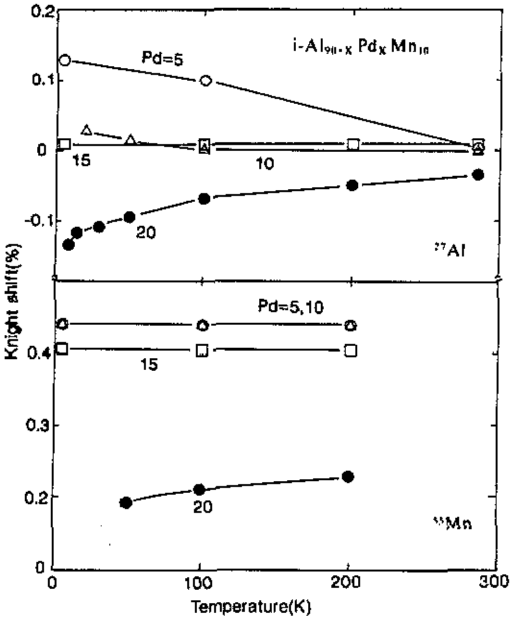

Figure 6. Knight shifts of ^{27}Al and ^{55}Mn nuclei in the Al–Pd–Mn quasicrystalline alloys. The numbers in the figure indicate the Pd contents.

shifts for $Al_{75}Pd_{15}Mn_{10}$, $Al_{80}Pd_{10}Mn_{10}$ and $Al_{85}Pd_5Mn_{10}$ may depend on whether the FCI phase exists or not.

Acknowledgments

The authors would like to thank T Sato for his assistance with the NMR measurements.

References

Carduner K R, Suits B H, Diverdi J A, Murphy V and White D 1987 *J. Mater. Res.* **2** 431
Edagawa K, Ino H, Nasu S, Kimura K, Takeuchi S, Sinjo J, Koga K, Shimizu T and Yasuoka H 1987 *J. Phys. Soc. Japan* **56** 2629
Eibschutz M, Lines M E, Chen H S and Wasczak J V 1988 *Phys. Rev.* B **38** 10038
Eibschutz M, Lines M E, Chen H S, Wasczak J V, Papaefthymion G and Frankel K B 1987 *Phys. Rev. Lett.* **59** 2443
Elser V 1985 *Phys. Rev.* B **32** 4892
Fukamichi K, Kikuchi K, Hattori Y, Tsai A P, Inoue A, Masumoto T and Goto T 1991a *Proc. China–Japan Joint Semin. on Quasicrystals* ed K H Kuo and T Ninomiya (Singapore: World Scientific) p 256
—— 1991b private communication
He L X, Wu Y K and Kuo K H 1988a *J. Mater. Sci. Lett.* **7** 1284
He L X, Zhang Z, Wu Y K and Kuo K H 1988b *Inst. Phys. Conf. Ser. 2* (Bristol: Institute of Physics) p 13
Rubinstein M, Stauss G H, Phillips T E, Moorjani K and Benett L H 1986 *J. Mater. Res.* **1** 243
Sainfort P, Dubost B and Dubus A 1985 *C. R. Acad. Sci., Paris* **10** 698
Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951
Tanaka M 1991 *Sci. Rep. Res. Inst. Tohoku Univ.* A **36** 159
Tsai A P, Chen H S, Inoue A and Masumoto T 1991 *Phys. Rev.* B **32** 4892

Tsai A P, Inoue A and Masumoto T 1987 *Japan. J. Appl. Phys.* **26** L1505
—— *1988 Japan. J. Appl. Phys.* **27** *L1587*
—— 1990a *Japan. J. Appl. Phys.* **29** L1161
—— 1990b *Phil. Mag. Lett.* **9** 62
Tsai A P, Inoue A, Yokoyama Y and Masumoto T 1990c *Mater. Trans. Japan Inst. Met.* **31** 98
Warren W W, Chen H S and Espinosa G P 1986 *Phys. Rev.* B **34** 4902
Warren W W, Chen H S and Hauser J J 1985 *Phys. Rev.* B **32** 7614
Yasuoka H, Soyama A, Kimura K and Takeuchi S 1986 *J. Phys. Soc. Japan* **55** 1058