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An NMR study of the new strong magnetism in the quasicrystalline Al–Pd–Mn–B system

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Abstract. We have measured ^{27}Al, ^{55}Mn and ^{11}B NMR spectra of the quasicrystalline Al–Pd–Mn–B system with the new strong magnetism. The zero-field spectra observed around 220 MHz at 4.2 K provide evidence that ferromagnetic Mn atoms exist in these icosahedral quasicrystals. Further, Mn atoms with no internal magnetic field are also detected in these icosahedral quasicrystals from spectra obtained in applied magnetic fields. From the microscopic point of view, by means of NMR, it is concluded that the icosahedral phase of this system consists of a magnetically heterogeneous atom distribution, although the x-ray diffraction pattern and transmission electron microscopy exhibit the formation of a single icosahedral phase in the Al–Pd–Mn–B alloy.

1. Introduction

Since the discovery of quasicrystals by Shechtman *et al* (1984), the magnetic properties of these materials have attracted considerable interest. Although most icosahedral quasicrystalline alloys (I alloys) have been reported to be diamagnetic, paramagnetic and spin-glass (O'Handley *et al* 1991, Stadnik *et al* 1989), it has recently been revealed from magnetization measurements that some Al-based I alloys possess ferromagnetism (Zao *et al* 1988, Tsai *et al* 1988, Dunlap *et al* 1989). The small value of the magnetization and the high Curie temperature of these alloys suggest the possibility that the weak ferromagnetism of these alloys may arise from a small amount of a second ferromagnetic phase (or phases). Especially, the origin of such magnetic behaviour has been investigated in Fe-doped Al–Cu–Ge–Mn I alloy by Mössbauer and x-ray diffraction experiments (Stadnik and Stronik 1991a, b, c, Miglierini and Nasu 1991, Nasu *et al* 1992). The data indicate that the hyperfine parameters of ^{57}Fe change only slightly below 50 K, and the ferromagnetism with a T_c of about 500 K results from a small amount of the ferromagnetic AlCuMn compound (Nasu *et al* 1992). However, the interpretation in cases with a strong magnetic field remains far from clear (see, for example, Srinivas *et al* 1990). For the other I phases there is much to be learned in order to understand fully the magnetic behaviour.

More recently, Yokoyama *et al* (1992) have carried out a systematic study in order to search for a new ferromagnetic quasicrystalline alloy with a large magnetization and high Curie temperature. As a result, they have found a single-quasicrystal phase with a significant magnetization in Al–Pd–Mn–B and Al–Cu–Mn–B systems. The temperature dependence of these inverse susceptibilities indicates a ferrimagnetic character. The magnetization value and Curie temperature depend on the composition and heat treatment; a phase transition from an I phase to a crystalline phase by annealing causes the disappearance of magnetization.

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The nuclear magnetic resonance (NMR) technique has provided unique local microscopic information about the structure and the magnetic properties of various materials. The purpose of this paper is to elucidate the source of the strong magnetism of I phases in the Al–Pd–Mn–B system by NMR measurements under zero and external magnetic fields.

2. Experimental details

Quaternary alloys with the composition of $Al_{50}Pd_{10}Mn_{25}B_{15}$ and $Al_{64}Pd_{15}Mn_{15}B_6$ were used in this study. These alloys were made by arc-melting a mixture of raw materials with a high purity (Al and Mn of 5N mass% purity, Pd of 4N and B of 3N) under an ambient argon atmosphere. Rapidly solidified ribbon samples with an icosahedral quasicrystal structure were prepared from the alloy ingots by using a single-roller melt-spinning apparatus. The quasicrystallinity of samples was examined by x-ray diffraction and transmission electron microscopy.

Figure 1 shows x-ray powder diffraction patterns of the melt-spun Al–Pd–Mn–B alloys. These patterns can be indexed in terms of Elser's index and show no visible trace from other phases. The value of magnetization at 20 kOe for $Al_{64}Pd_{15}Mn_{15}B_6$ and $Al_{50}Pd_{10}Mn_{25}B_{15}$ I alloys is 18.9 emu g^{-1} (0.97 μ_B/Mn) at 4.2 K and 34 emu g^{-1} (0.96 μ_B/Mn) at 77 K, respectively (Yokoyama *et al* 1992, 1993).

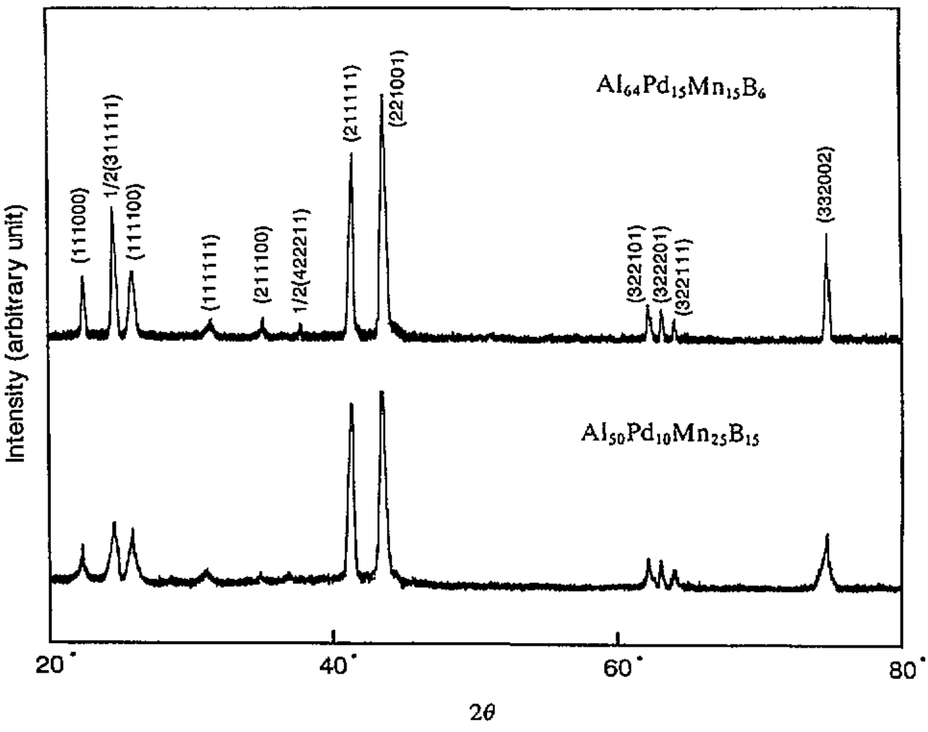

Figure 1. X-ray diffraction patterns of icosahedral quasicrystalline $Al_{64}Pd_{15}Mn_{15}B_6$ and $Al_{50}Pd_{10}Mn_{25}B_{15}$ alloys.

For observation of NMR signals, a conventional pulsed NMR spectrometer was utilized. Zero-field measurements have been performed at 4.2 K in the frequency range between 20 MHz and 270 MHz. From Mössbauer and NMR measurements, it has been pointed out that two classes of transition metal site exist in the Curie–Weiss-type paramagnetic I-alloys. Thus, we tried to search for paramagnetic NMR signals at a fixed radiofrequency by sweeping external field.

3. Results and discussion

For $Al_{64}Pd_{15}Mn_{15}B_6$ and $Al_{50}Pd_{10}Mn_{25}B_{15}$ I alloys, spin echo signals in zero field were detected at 4.2 K in the wide frequency range between 20 and 250 MHz. The spectra obtained show two intense peaks around 35 and 220 MHz (figures 2 and 3). The peak around 220 MHz, accompanied by its satellites, is naturally considered to be due to the Mn sites with a ferromagnetically ordered moment by comparing with the resonance frequencies of ^{55}Mn reported for many intermetallic Mn compounds (Turov and Petrov 1972). The peak around 35 MHz is likely to be due to B sites because its intensity decreases with decreasing B content. The overall features of these spectra are similar in the two alloys and the compositional effect on the line width is not found for these alloys. Although there are no distinct peaks in zero field except for the above two intense peaks, weak echo signals prevailed over the measured frequency range. These signals are attributable to the Al sites distributed at different distances away from the ferromagnetic Mn atoms because of the abundance of the Al atoms. These results imply that the strong magnetism comes from the existence of ferromagnetic Mn atoms with a significant magnetic moment, contrary to the ferrimagnetism expected from the magnetization measurements; Mn atoms with two different magnetic moments couple antiferromagnetically (Yokoyama *et al* 1992).

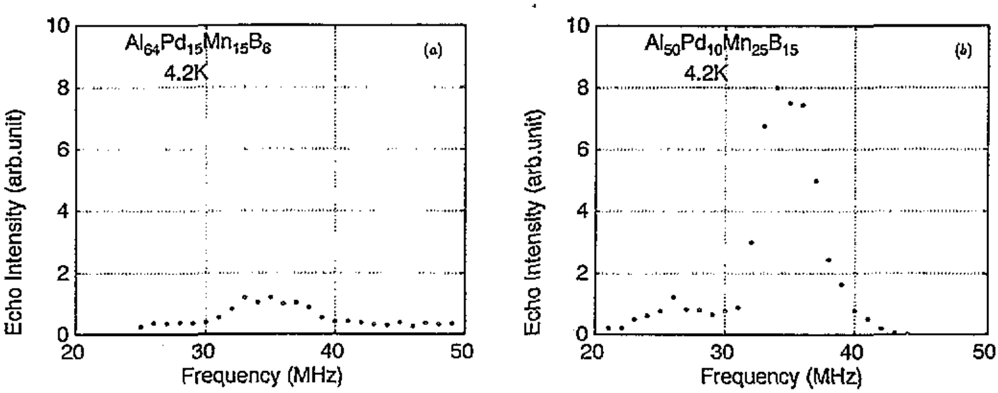

Figure 2. Zero-field spin-echo spectra around 35 MHz at 4.2 K for icosahedral (*a*) $Al_{64}Pd_{15}Mn_{15}B_6$ and (*b*) $Al_{50}Pd_{10}Mn_{25}B_{15}$ alloys.

It is necessary to consider whether these two distinct peaks result from the crystal MnB precipitated in these I alloys since the frequencies of these peaks show a good coincidence with those from Mn and B sites in the intermetallic compound MnB (Hihara and Hirahara 1965). We then measured a zero-field spectrum of MnB which was prepared by arc-melting. Figure 4 shows that both Mn and B signals in this compound form a single sharper peak

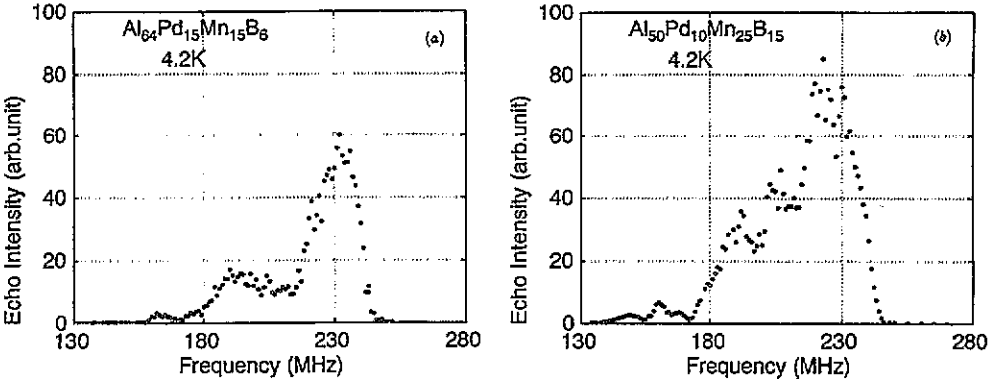

Figure 3. Spin-echo spectra around 220 MHz at 4.2 K for icosahedral (*a*) $Al_{64}Pd_{15}Mn_{15}B_6$ and (*b*) $Al_{50}Pd_{10}Mn_{25}B_{15}$ alloys under no magnetic field.

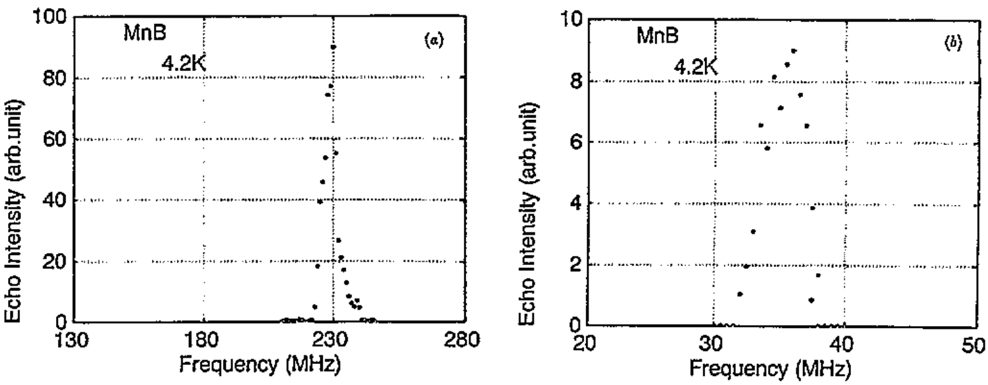

Figure 4. Spin-echo spectra of the intermetallic compound MnB, (*a*) Mn and (*b*) B, in zero external magnetic field at 4.2 K.

as compared with those in I alloys. In fact, the peak frequencies are in good agreement with those in I alloys. However, the peak intensity of the Mn spectra for these I alloys is comparable to that in the crystal MnB and weakly broadened NMR signals from Al exist. Moreover, there exists no other phase in diffraction measurements for these I alloys. Therefore, it is concluded that the two intense peaks of observed spectra evidently result from sites with MnB-like bonding. The satellite peaks near 220 MHz can be considered to come from imperfect MnB-like bonding (see, for example, Budnick *et al* 1985). For clarification, measurements of magnetic field effect on these spectra will be needed. The above results seem to indicate that the proportionality of the number of MnB-like sites with Mn and B content reflects the increase of magnetization of this system. The value of magnetization estimated from the resonance frequency of ^{55}Mn ($\sim 2\mu_B$ by using a hyperfine coupling constant of 125 MHz/μ_B) is significantly different from that ($\sim 1\mu_B$) obtained from the magnetization measurements.

Two classes of Mn sites exist in the paramagnetic I alloys as reported previously (Warren *et al* 1986, Edagawa *et al* 1987, Eibschutz *et al* 1987). Thus, we investigated whether or not paramagnetic signals are observed. Figure 5 shows field-swept spectra of ^{11}B, ^{27}Al and ^{55}Mn at a fixed radiofrequency (36.000 MHz) at 5 K. These spectra indicate the existence of non-magnetic Mn atoms (considered to carry no localized magnetic moment as described later) in these I alloys, similar to that in the paramagnetic I alloy of $Al_{70}Pd_{20}Mn_{10}$ (Shinohara *et al* 1992, 1993a, b). The intensity of the ^{27}Al and ^{55}Mn signals becomes weaker for the $Al_{50}Pd_{10}Mn_{25}B_{15}$ than for the $Al_{64}Pd_{15}Mn_{15}B_{6}$ I alloy reflecting the broadening of the spectra; that of the ^{11}B signal exhibits the opposite behaviour presumably because of different B content. Comparing with the zero-field spectra, these field-swept spectra are attributable to the nuclei distant from the ferromagnetic MnB-like sites.

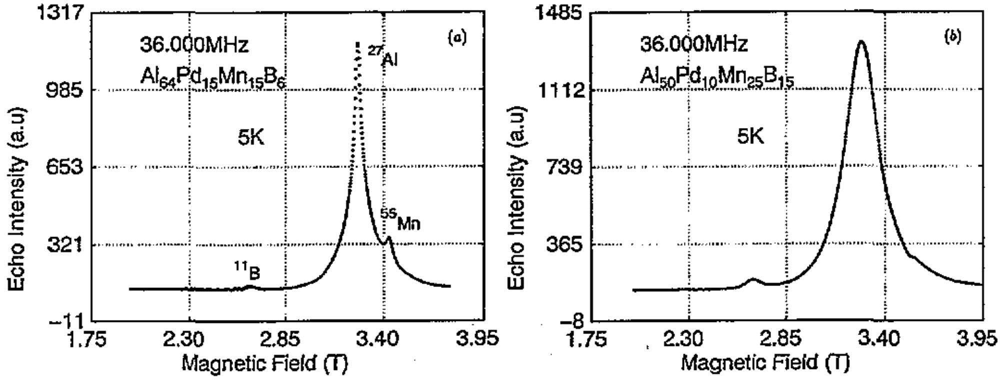

Figure 5. ^{11}B, ^{27}Al and ^{55}Mn spin-echo spectra observed at 5 K at 36.000 MHz in a sweeping magnetic field.

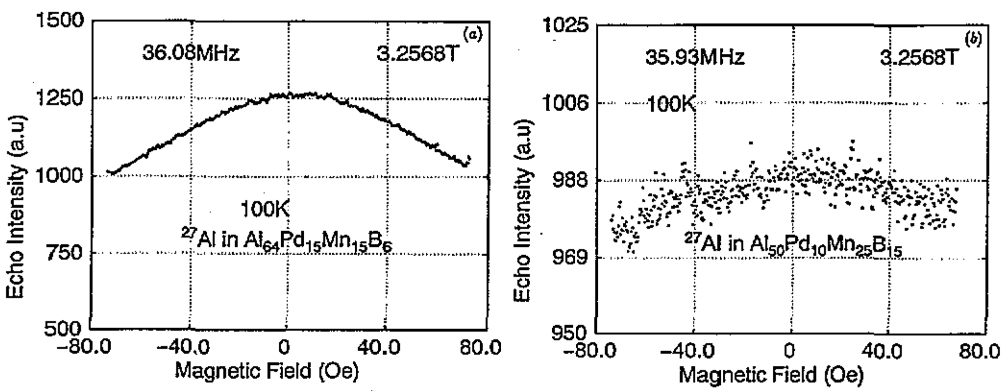

Figure 6. ^{27}Al spin-echo spectra obtained at 100 K at a fixed radiofrequency (denoted in the figure) in a sweeping magnetic field in the narrow range. The magnetic field from the superconducting magnet is denoted in the figure.

Further, we measured the temperature dependence of spectra in a narrow field range, in order to obtain the peak shift precisely (for example, figure 6). The obtained values of

Table 1. Knight shift data for ^{27}Al, ^{55}Mn and ^{11}B.

Temperature (K)	$Al_{64}Pd_{15}Mn_{15}B_6$	$Al_{50}Pd_{10}Mn_{25}B_{15}$
	^{27}Al Knight shift data (%)	
10	$-0.16+0.01$	$-0.62+0.02$[a]
100	$-0.14+0.01$	$-0.57+0.02$
200	$-0.13+0.01$	$-0.49+0.02$
295	$-0.09+0.01$	—
	^{55}Mn Knight shift data (%)	
Temperature (K)	$Al_{64}Pd_{15}Mn_{15}B_6$	$Al_{50}Pd_{10}Mn_{25}B_{15}$
10	$+0.25+0.02$	$-0.20+0.02$
100	$+0.25+0.02$	—
200	$+0.27+0.02$	—
	^{11}B Knight shift data (%) at 5 K	
	$Al_{64}Pd_{15}Mn_{15}B_6$	$Al_{50}Pd_{10}Mn_{25}B_{15}$
	$-0.42+0.20$	$-0.93+0.20$

[a] Data at 50 K.

the ^{27}Al, ^{55}Mn and ^{11}B Knight shifts at various temperatures are tabulated in table 1. The ^{27}Al Knight shift values of both I alloys are negative. This fact may be interpreted from the presumption that the number of MnB-like ferromagnetic sites and the contribution from conduction electron polarization by RKKY interaction increase in these alloys, corresponding to the large magnetization. For the $Al_{64}Pd_{15}Mn_{15}B_6$ I alloy, the ^{55}Mn Knight shift has a temperature-independent positive value due to orbital contribution and conduction electron polarization. Such Mn atoms bear no localized moment, because the inner core polarization, generating much negative shift, cannot be considered. If this is the case, these magnetically different Mn atoms may cause the composition-dependent difference between the ferromagnetic Curie temperature and the asymptotic Curie temperature. Yokoyama *et al* (1992, 1993) have indicated that the difference for these alloys is due to ferrimagnetic coupling. The coexistence of ferromagnetic and non-magnetic Mn atoms in a structurally single phase is characteristic for these I alloys. Such a magnetically heterogeneous phase has been reported by NMR measurements for the other magnetic substance $Co(S_xSe_{1-x})_2$ (Inoue *et al* 1981). However, the origin of the above magnetically different Mn atoms is not easy to identify until the atomic order is determined.

Besides, paramagnetic Mn atoms with a local magnetic moment may coexist in these I alloys, for similar reasons to those applying to other I alloys (Warren *et al* 1986, Shinohara *et al* 1992, 1993a, b). But no trace from these atoms can be found in the present NMR spectra.

From the fact that the line width in the x-ray diffraction pattern becomes broad with the increase of magnetization, Yokoyama *et al* (1993) have pointed out that the generation of magnetization in this I-alloy system closely correlates to the existence of strain. Unfortunately, neither the amount of Al and Mn atoms with no internal field, nor the amount of ferromagnetic Mn atoms, in these I alloys can be estimated in this study. In a previous paper, we have reported that the $Al_{75}Pd_{15}Mn_{10}$ I alloy is Pauli-type paramagnetic whereas $Al_{73}Pd_{15}Mn_{12}$ shows Curie–Weiss-type paramagnetism (Shinohara *et al* 1992, 1993a, b). If we simply assume that the substitution of Mn for Al produces strain and generates magnetic moments of Mn, a ferromagnetic Mn atom could carry a magnetic moment of 2.7 μ_B/atom in

$Al_{64}Pd_{15}Mn_{15}B_6$, being 3/2 times larger than the value expected from the internal hyperfine field. This rough estimate seems to suggest a possibility of there being Mn atoms with a large magnetic moment. If the orbital moment could contribute, the magnetic moment deduced from the internal field may be larger.

4. Summary

In order to elucidate the source of the strong magnetism observed in the new quasicrystalline I alloys, $Al_{64}Pd_{15}Mn_{15}B_6$ and $Al_{50}Pd_{10}Mn_{25}B_{15}$, we have measured the NMR spectra in zero and external fields. The results obtained are summarized as follows.

(i) Under zero field, the spectra show two intense peaks due to the Mn and the B. Besides, the weak signals due to the Al were observed in a wide frequency range in zero magnetic field.

(ii) However, the same samples exhibit the presence of the ^{11}B, ^{27}Al and ^{55}Mn atoms with no internal magnetic field, showing the Knight shift due to the conduction electron polarization through RKKY interaction with the ferromagnetic Mn atoms.

(iii) From the microscopic point of view, the indication that the strong magnetism in these I alloys is due to a ferrimagnetic coupling should be corrected: the coexistence of ferromagnetic and non-magnetic Mn atoms in a structurally single phase is characteristic of the present I alloys.

(iv) Although the X-ray diffraction shows a single phase in these I alloys, it is to be noted that the ferromagnetism comes from a heterogeneous magnetic atom distribution with the partial lattice distortion.

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References

Budnick J I and Burch T J 1985 *Hyperfine Interact.* **24–6** 377
Dunlap R A, McHenry M E, Srinivas V, Bahadur D and O'Handley R C 1989 *Phys. Rev.* B **39** 4808
Edagawa K, Ino H, Nasu S, Kimura K, Takeuchi S, Shinjo T, Koga K, Shimizu T and Yasuoka H 1987 *J. Phys. Soc. Japan* **56** 2629
Eibschutz M, Lines M E, Chen H S, Waszczak J V, Papaefthymiou G and Frankel R B 1987 *Phys. Rev. Lett.* **59** 2443
Hihara T and Hirahara E 1965 *J. Phys. Soc. Japan* **20** 873
Inoue N, Yasuoka H, Matsui M and Adachi K 1981 *J. Phys. Soc. Japan* **50** 1180
Miglierini M and Nasu S 1991 *J. Phys. Soc. Japan* **60** 2135
Nasu S, Miglierini M and Kuwano T 1992 *Phys. Rev.* B **45** 12778
O'Handley R C, Dunlap R A and McHenry M E 1991 *Handbook of Magnetic Materials* vol 6, ed K H J Buschow (Amsterdam: Elsevier–North-Holland) p 453
Shechtman D, Blech I, Gratis D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951
Shinohara T, Tsai A P and Masumoto T 1992 *J. Phys.: Condens. Matter* **4** 3043
—— 1993 *Hyperfine Interact.* at press
Shinohara T, Tsai A P, Masumoto T and Sato T 1993b *Mater. Trans. Japan. Inst. Met.* **34** 146
Srinivas V, Dunlap R A, McHenry M E and O'Handley 1990 *J. Appl. Phys.* **67** 5879
Stadnik Z M and Stronik G 1991a *Hyperfine Interact.* **69** 643
—— 1991b *Phys. Rev.* B **43** 894

—— 1991c *Phys. Rev.* B **44** 4255
Stadnik Z M, Stronik G, Ma H and Williams G 1989 *Phys. Rev.* B **39** 9797
Tsai A P, Inoue A, Masumoto T and Kataoka N 1988 *Japan. J. Appl. Phys.* **27** L2252
Turov E A and Petrov M P 1972 *Nuclear Magnetic Resonance in Ferro- and Antiferromagnets* (New York: Wiley–Halted)
Warren W W, Chen H S and Espinosa G P 1986 *Phys. Rev.* B **34** 4902
Yokoyama Y, Inoue A and Masumoto T 1992 *Mater. Trans. Japan. Inst. Met.* **31** 98
Yokoyama Y, Yamauchi H, Inoue A and Masumoto T 1993 to be submitted
Zao J G, Yang L Y, Fu Q and Guo H Q 1988 *Mater. Trans. Japan. Inst. Met. Suppl.* **29** 497