Magnetic and Mössbauer studies of quasicrystalline Al$_{70-x}$Pd$_{15}$T$_{15}$M$_x$  

(T = Mn, Fe; M = Si, Ge; 0 ≤ x ≤ 8)

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Abstract

Our magnetisation and Mössbauer effect investigations of magnetic icosahedral quasicrystals (Al, Ge)$_{70}$Pd$_{15}$Mn$_{15}$ and (Al, Si)$_{70}$Pd$_{15}$Fe$_{15}$ have shown that the magnetic atoms Mn and Fe occupy two types of sites, one of which is magnetic and one which is non-magnetic. In certain cases the magnetic atoms couple ferromagnetically.

Keywords: Quasicrystals; Magnetisation; Mössbauer effect; Icosahedral

1. Introduction

The moment formation in Al-based quasicrystals when 3D (Fe/Mn/Cr/Co) and 4D (Pd) magnetic atoms are simultaneously present has recently been studied [1–4] Evidence of magnetic ordering in such alloys have also been reported when metalloid such as Boron or Germanium is used as a fourth component [4–6]. However, a clear understanding of the magnetic behaviour of these alloys is not yet available.

Yokoyama et al. [4] and Bahadur et al. [5] have studied the magnetic properties of Al-Pd-Mn-B icosahedral quasicrystals and have concluded that the Mn atoms occupy two types of sites, on one of which it has no moment while on the other it has a small moment that can enter into ferromagnetic interactions with its near neighbours through an indirect coupling of 3D moments. The moment formation has been explained on the basis of Anderson’s model of localised magnetic states in metals [5]. On replacing B by Si or Ge the changes in lattice constant are expected. The magnetic moment formation when a magnetic atom T (Mn or Fe) is introduced in a non-magnetic matrix Al-M (M = metalloid) is not understood at present and efforts have been made to study this problem for a fixed value of T and Pd. In the present study we have synthesised Al$_{70-x}$Pd$_{15}$T$_{15}$M$_x$ (M = Si, Ge; 0 ≤ x ≤ 10; T = Mn, Fe) by melt spinning. These alloys have been characterised by X-ray diffraction, room temperature Mössbauer spectroscopy and magnetic susceptibility measurements in the temperature range 4 to 300 K.

2. Experimental methods

Alloys of composition Al$_{70-x}$Pd$_{15}$T$_{15}$M$_x$ with 0 ≤ x ≤ 10, M = Si; Ge, T = Mn, Fe were prepared by rapid quenching from the melt. X-ray diffraction measurements were made on a Siemens D-500 scanning diffractometer using Cu Kα radiation. Magnetic susceptibility measurements were carried out between 4 and 300 K in applied fields of 1T using a SQUID magnetometer. Room temperature $^{57}$Fe Mössbauer measurements were made using a Pd$^{57}$Co source and a Wissel System II spectrometer with an intrinsic $^{57}$Fe line width of 0.23 mm s$^{-1}$ (FWHM).

3. Results and discussion

X-ray diffraction results show that all samples are single-phase icosahedral alloys. Fig. 1 shows the plot of quasilattice constant versus metalloid concentration in Al$_{70-x}$Pd$_{15}$T$_{15}$M$_x$ (T = Mn, Fe; M = Ge, Si; x values between 0 and 10). This plot shows that on substituting Si for Al, the lattice parameter decreases linearly with increasing Si content and follows Vegard’s law. On the other hand, on substituting Ge for Al, the lattice constant remains almost unchanged as has been reported elsewhere [4]. This effect may be readily understood on the basis of the similarity of the ionic radii of Al$^{3+}$ and Ge$^{4+}$ (0.51 and 0.5 Å), respectively, and the much smaller ionic radius of Si$^{4+}$ (0.42 Å). The change from Mn to Fe lowers the quasilattice constant by nearly 0.06 Å. The room temperature Mössbauer spectra of Al$_{70-x}$Fe$_{15}$Pd$_{15}$M$_x$ (M = Si, Ge, 2 ≤ x ≤ 10) exhibit
only a well defined doublet like the system with boron (6). However at 4.2 K the Mössbauer spectrum of B containing alloy shows hyperfine split component superposed on doublet at 4.2 K and hysteresis at both 4.2 and 300 K in fields −1T to +1T.

A plot of the variation of centre shift (CS) and quadrupole splitting (QS) is given in Fig. 2. In $0 \leq x < 10$ range, the CS for Ge alloys does not change significantly while for large values of $x$, Si based alloys show a significant change. This agrees with the fact that the lattice contracts on Si substitution while it remains unaffected on Ge substitution.

Our results show that $CS = +0.200 \text{mm s}^{-1}$ for Al$_{62}$Fe$_{15}$Pd$_{15}$Si$_{8}$, which is substantially smaller than for Fe atoms in the metallic ordered state. This shows that the local electronic structure around Fe atom in the present alloy is different from Fe in the ordered magnetic state. The QS for this sample is $0.408 \text{mm s}^{-1}$. This is small compared with $0.454 \text{mm s}^{-1}$ reported for Al$_{62}$Fe$_{15}$Pd$_{15}$Si$_{8}$ [6]. The CS for Al$_{60}$Fe$_{15}$Pd$_{15}$Ge$_{10}$ is $+0.259 \text{mm s}^{-1}$ and the QS is $0.373 \text{mm s}^{-1}$, similar to the Si based alloy.

In Fig. 3 we have shown the temperature dependence of susceptibility for: (a) Al$_{62}$Mn$_{15}$Pd$_{15}$Ge$_{8}$; (b) Al$_{62}$Fe$_{15}$Pd$_{15}$Ge$_{2}$; (c) Al$_{62}$Fe$_{15}$Pd$_{15}$Ge$_{6}$; (d) Al$_{60}$Mn$_{15}$Pd$_{15}$Si$_{2}$ and (e) Al$_{62}$Mn$_{15}$Pd$_{15}$Si$_{8}$ in the range $4 \text{K} < T < 350 \text{K}$. For (a) and (e) the susceptibility shows nearly Curie–Weiss like behaviour while for (d) the curve appears to be superposition of two Curie–Weiss curves. The data is fitted to $\chi = \chi_0 + C/(T - \theta)$ and values of $C$, $\theta$ and the fraction $N^s/N$ of the magnetic Mn atoms for these alloys have been obtained. The Curie constant $C = N\mu_{\text{eff}}/3K_B$ gives the effective moments. The values of $\mu_{\text{eff}}$ are obtained assuming that the Mn atoms are in high spin state ($S = 5/2$).

Table 1 gives the calculated values of $\mu_{\text{eff}}$ and $N^s/N$. We have taken $\mu_{\text{eff}} = g[S(S + 1)]^{1/2} \mu_B$ the quantum mechanical value for the magnetic moment with $g = 2$ and $S = 2.5$ for Si containing alloys and $g = 2$ and $S = 2.7$ for Ge containing alloy.

The values of $\mu_{\text{eff}}$ obtained are contrary to the values reported for Al$_{70}$Pd$_{20}$Mn$_{2x}$Fe$_{10-x}$ [1] and Al$_{74}$Mn$_{20-x}$Fe$_{x}$Si$_{6}$ [7], which are in 1.5–1.9 $\mu_B$ range. On the other hand, this
agrees with the conclusions of Lasjaunias et al. [2] who find that in quasicrystalline — Al_{68.7}Pd_{21.7}Mn_{9.6} only a few Mn atoms carry a large spin ($S \sim 3.3$) which are coupled by RKKY interaction yielding a spin glass transition close to 1.0 K. So the value of $S$ close to 2.5 assumed in the present case is justified. The presence of 100% magnetic Mn atoms in Al$_{62}$Pd$_{15}$Mn$_{15}$Ge$_8$ is against the suggestion that in these alloys there are two distinct types of sites; one magnetic and the other non-magnetic [7,8] which agrees even with our data on Al-Pd-Mn-Si compounds. Similar observations on Al$_{60}$Ge$_{10}$Pd$_{12.5}$Mn$_{17.5}$ alloy reported by Lin et al. [3] have been interpreted as arising from two magnetic state sites, one giving a paramagnetic and the other a ferromagnetic contribution. They ascribe the paramagnetic component to quasicrystalline Al-Ge-Pd-Mn and the ferromagnetic component to crystalline Al-Ge-Mn. Due to the complexity of the problem they have not made any attempt to estimate the relative fraction of the paramagnetic and ferromagnetic components.

The plot of susceptibility for (b) and (c) in Fig. 3 shows a small variation with temperature in the range 4 < $T$ < 290 K and a Curie–Weiss like behaviour above 290 K. In these compounds the moments are field-induced and tend to vanish when the external field vanishes. In our ferromagnetic resonance studies of icosahedral Al-Mn-Pd-B alloys [5] we have shown that local moments form on some Mn sites and are coupled through boron atoms when neighbouring icosahedra are in a specific edge-sharing configuration. We expect this to also take place in Al-Mn-Pd-M (M = Ge, Si) alloys. The dependence of susceptibility on temperature in these Al-Pd-Fe-M alloys shows two maxima, one at $T < T_c$ and the other at $T = T_c$. This is similar to that observed in high permeability ferrites [9]. The first maximum occurs close to where the anisotropy field, $H_A$, vanishes and the other occurs near $T_c$. In a study of the effect of addition of B and Ge in Al-based quasicrystals with appropriate Mn content Yokoyama et al. [4] have found that ferromagnetism appears on addition of metalloids like B and Ge and the coercivity increases when B is replaced by Ge. The observed difference in magnetic behaviour of Al-Pd-Mn-M and Al-Pd-Fe-M alloys can thus be explained on the basis that the ferrimagnetic component in Al-Pd-Fe-M alloy dominates the paramagnetic component while the reverse happens in the Al-Pd-Mn-M alloys.

4. Conclusion

It is observed that the presence of Si and Ge in the Al-Pd-Mn and Al-Pd-Fe icosahedral phases affects the magnetic properties differently. The Si containing Al-Pd-Mn alloys have only small percentage of magnetic atoms which do not couple ferromagnetically. On the other hand 8% Ge containing Al-Pd-Mn alloy produces 100% paramagnetic Mn atoms. The Al-Pd-Fe-Ge alloys show ferromagnetic behavior within the temperature 4–290 K range.

References