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Spin-glass behaviour of icosahedral Mg–Gd–Zn and Mg–Tb–Zn quasi-crystals

Y Hattori†, A Niikura‡, A P Tsai‡, A Inoue‡, T Masumoto‡, K Fukamichi†, H Aruga-Katori§ and T Goto§

† Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980-77, Japan
‡ Institute for Materials Research, Tohoku University, Sendai 980-77, Japan
§ Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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Abstract. The magnetic properties of icosahedral $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) quasi-crystals have been investigated. These quasi-crystalline phases have a face-centred icosahedral lattice with a highly ordered Frank–Kasper-type structure as identified by electron diffraction and x-ray diffraction. The temperature dependence of DC magnetic susceptibility obeys a Curie–Weiss law in wide temperature ranges. The effective magnetic moments μ_{eff} are close to those of free RE^{3+} ions and their paramagnetic Curie temperature Θ_p is negative, indicating that the RE–RE exchange interactions are predominantly antiferromagnetic. The value of Θ_p which is the sum of all exchange interactions is almost in proportion to the de Gennes factor. At low temperatures, spin-glass behaviour has been observed in the icosahedral $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasi-crystals and their spin freezing temperatures T_f are 5.5 K and 7.6 K, respectively.

1. Introduction

Since the discovery of an Al–Mn quasi-crystal (Shechtman *et al* 1984), many high-quality Al-based quasi-crystals have been developed (Sainfort and Dubost 1986, Tsai *et al* 1987, 1989, 1990, 1991) and characteristic physical properties for these quasi-crystals have been investigated (Akiyama *et al* 1993, Lanco *et al* 1993, Suck 1993). On the other hand, it is well known that the magnetic properties of alloys containing a magnetic element are very sensitive to their local atomic structures such as the kinds of nearest-neighbour atom, the atomic distance and the coordination number. Therefore, the magnetic properties of quasi-crystals would be different from those of amorphous alloys in spite of the similarity of both local atomic structures (Matsubara *et al* 1988). Accordingly, the magnetic properties of Al–Cu–Mn and Al–Pd–Mn alloys in the quasi-crystalline and amorphous states have been systematically investigated and a clear distinction between the two states has been confirmed (Fukamichi *et al* 1991, 1993, Hattori *et al* 1994). The magnetic susceptibility exhibits a Curie–Weiss-type temperature dependence for the single-grained $Al_{68}Pd_{23}Mn_9$ quasi-crystal (Matsuo *et al* 1993) and the polygrained Al–Mn, Al–Cu–Mn and Al–Pd–Mn quasi-crystals (Fukamichi *et al* 1987, 1991, 1993, Hattori *et al* 1994). Moreover, spin-glass behaviour has been confirmed for quasi-crystalline Al–Mn, Al–Cu–Mn and Al–Pd–Mn alloys (Fukamichi *et al* 1987, 1991, 1993, Hattori *et al* 1994).

Recently, quasi-crystals have been reported to be formed in Mg–Y–Zn and Mg–mischmetals–Zn systems (Luo *et al* 1993, Tang *et al* 1993). However, these quasi-crystalline

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phases coexist with a large amount of other crystalline phases. Subsequently, $Mg_{45}RE_5Zn_{50}$ (RE ≡ Tb, Dy, Ho or Er) and $Mg_{45}Y_5Zn_{50}$ quasi-crystals which are classified as a Frank–Kasper type have been found to be thermodynamically stable and have a highly ordered face-centred icosahedral lattice (Niikura *et al* 1994a). Further, the systematic work has revealed that the ideal composition of these stable quasi-crystals is close to $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) and $Mg_{42}Y_8Zn_{50}$ in a conventional solidification (Tsai *et al* 1994). No studies of magnetic properties of the $Mg_{42}RE_8Zn_{50}$ quasi-crystals have ever been carried out. Therefore, it is interesting to investigate the magnetic properties for the single phase of these quasi-crystals. In particular, the development of a spin-glass state is expected owing to the large magnetic moment of the heavy rare-earth element, despite the lower content of magnetic element than that in Al-based quasi-crystals such as $Al_{80}Mn_{20}$, $Al_{80-x}Cu_{20}Mn_x$ and $Al_{85-x}Pd_{15}Mn_x$ ($x = 13$, 14 and 15) (Fukamichi *et al* 1987, 1991, 1993, Hattori *et al* 1994). In the present paper, therefore, the magnetic properties of icosahedral quasi-crystalline phases of $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) alloys have been investigated after confirming their quasi-crystalline structure.

2. Experimental details

The quasi-crystalline samples with nominal compositions of $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) were prepared using starting materials of 99.9 wt% RE, 99.99 wt% Mg and 99.99 wt% Zn by induction melting in a pyrolytic boron nitride crucible in an argon gas atmosphere. The quasi-crystalline state was confirmed by powder x-ray diffraction using Cu Kα radiation and by transmission electron microscopy (TEM). The samples for TEM observation were crushed in alcohol and then transferred to a carbon grid. The compositional analysis was made by an inductively coupled plasma method. The powder samples were used for the magnetic measurements. The temperature dependence of the DC magnetic susceptibility was measured using an extraction-type magnetometer with a superconducting magnet. The field dependence of magnetization up to 55 kOe and the magnetic field cooling effect were measured with a SQUID magnetometer (Quantum Design, MPMS). The measurement of the AC magnetic susceptibility was performed by a mutual induction method at a frequency of 80 Hz in an AC magnetic field of 10 Oe.

3. Results and discussion

The analysed compositions scarcely deviate from the nominal compositions; the difference between the concentrations of non-magnetic elements is less than 0.8 at.%, and the concentrations of magnetic rare-earth elements of 7.8 at.% are the same as shown in table 1. Because the analysed compositions exhibit a very small deviation from the nominal compositions, we use the nominal compositions in the present paper.

Table 1. Nominal and analysed compositions of the Mg–Gd–Zn, Mg–Tb–Zn and Mg–Dy–Zn quasi-crystals.

Nominal	$Gd_8Mg_{42}Zn_{50}$	$Tb_8Mg_{42}Zn_{50}$	$Dy_8Mg_{42}Zn_{50}$
Analysed	$Gd_{7.8}Mg_{42.5}Zn_{49.7}$	$Tb_{7.8}Mg_{42.8}Zn_{49.4}$	$Dy_{7.8}Mg_{42.4}Zn_{49.8}$

Figures 1(a), (b) and (c), show the x-ray diffraction patterns of the $Mg_{42}Gd_8Zn_{50}$, $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Dy_8Zn_{50}$ alloys respectively, in the as-cast state. Almost all peaks can be indexed by a set of icosahedral indices using Elser's (1985) method, although the indices are given to only main peaks. Similar x-ray diffraction patterns have been obtained for $Mg_{42}Ho_8Zn_{50}$ and $Mg_{42}Er_8Zn_{50}$ alloys (Tsai *et al* 1994). The icosahedral quasi-crystals are known to be classified into two groups. The icosahedral Al–TM (TM ≡ transition metal) phases of a Mackay icosahedron type have a quasi-lattice of about 0.46 nm and a valence concentration (electron-to-atom ratio) of about 1.75, while these values for icosahedral phases of a Frank–Kasper type are about 0.52 nm and about 2.1, respectively. The lattice parameter determined from the (211111) peak is 0.5222 nm for $Mg_{42}Gd_8Zn_{50}$, 0.5199 nm for $Mg_{42}Tb_8Zn_{50}$ and 0.5187 nm for $Mg_{42}Dy_8Zn_{50}$, decreasing with the decrease in the atomic radius of the lanthanoid metals (Gd > Tb > Dy) (Tsai *et al* 1994). These lattice constants reveal that the present icosahedral phases are of the Frank–Kasper type. The diffraction peaks of these icosahedral phases which show a very high ordered quality, are very sharp, i.e. the value of the half-width at half-maximum of the (211111) peak is approximately 0.05 nm^{-1} for $Mg_{42}Gd_8Zn_{50}$, being smaller than that of about 0.08 nm^{-1} for icosahedral $Al_5Li_3Cu_1$ prepared by a Bridgmann growth method (Chen *et al* 1988). As seen from the figure, the superlattice peaks of $\frac{1}{2}(111111)$ and $\frac{1}{2}(233111)$ which indicate the face-centred icosahedral structure have been reported (Tsai *et al* 1994). It is interesting to note that the primitive icosahedral lattice has been obtained by rapid solidification for $Mg_{40}RE_5Zn_{55}$ alloys (Niikura *et al* 1994b).

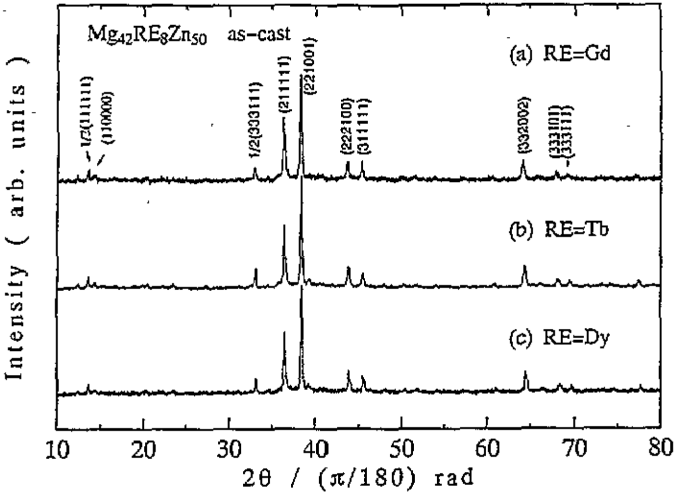

Figure 1. X-ray diffraction patterns of the $Mg_{42}Gd_8Zn_{50}$, $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Dy_8Zn_{50}$ quasi-crystals.

Figures 2(a), 2(b) and 2(c) show the selected-area diffraction patterns of icosahedral $Mg_{42}Gd_8Zn_{50}$ with incident beams along the fivefold, threefold and twofold axes, respectively. The patterns exhibit many very fine spots, and the deviation and the distortion of reflections from the ideal icosahedral symmetric positions owing to phason strains are as small as those for icosahedral Al–Cu–Fe with a very high quality (Tsai *et al* 1987). We have also observed the innermost spots corresponding to a long-range correlation of 24.3 nm in a twofold pattern. Therefore, it is clear that the $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or

Er) alloys are face-centred icosahedral quasi-crystals with a very high quality in a similar manner to icosahedral $Al_{70}Pd_{20}Mn_{10}$ (Tsai *et al* 1991). From these structural studies, it is considered that the present quasi-crystals are appropriate for the investigation of magnetic properties.

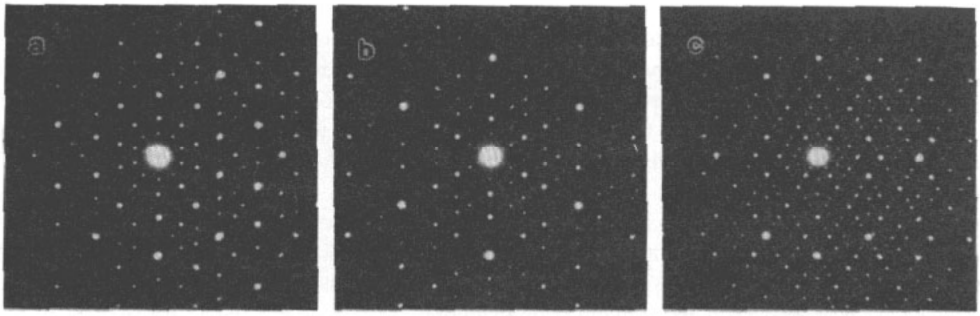

Figure 2. Electron diffraction patterns of the quasi-crystalline $Mg_{42}Gd_8Zn_{50}$ alloy taken by the incident beams parallel to (a) the fivefold, (b) the threefold and (c) the twofold axes.

Figure 3 shows the temperature dependence of DC magnetic susceptibility χ_{DC} for $Mg_{42}Gd_8Zn_{50}$, $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Dy_8Zn_{50}$ quasi-crystals. All these exhibit a Curie–Weiss-type temperature dependence. The effective magnetic moment μ_{eff} and the paramagnetic Curie temperature Θ_p are obtained from the following conventional equation:

$$\chi - \chi_0 = \frac{N\mu_{eff}^2}{3k_B} \tag{1}$$

where χ_0 is the temperature-independent susceptibility, N the number of RE atoms per mole and k_B the Boltzmann constant. The values of μ_{eff} are close to those of free RE^{3+} ions. In these quasi-crystals, therefore, all RE atoms are considered to have a localized magnetic moment, although there are magnetic and non-magnetic Mn atoms in Al–Mn (Warren *et al* 1986, Goto *et al* 1988), Al–Cu–Mn and Al–Pd–Mn (Fukamichi *et al* 1991, 1993, Hattori *et al* 1994) quasi-crystals. The present quasi-crystalline alloys exhibit a negative value of Θ_p, showing that the RE–RE exchange interactions are predominantly antiferromagnetic. Figure 4 displays Θ_p for $Mg_{42}RE_8Zn_{50}$ (RE $\equiv$ Gd, Tb, Dy, Ho or Er). The magnitude of Θ_p which is sum of all exchange interactions varies almost in proportion to the de Gennes factor $\xi = c(g-1)^2J(J+1)$, where c, g and J are the content of magnetic element, the Landé g-factor and the total angular momentum, respectively.

In low-temperature ranges, the DC magnetic susceptibility χ_{DC} deviates from the Curie–Weiss law as seen from figure 3, suggesting the existence of magnetic ordering. It should be noted that spin freezing occurs when their effective magnetic moment is larger than about $(0.8-1)\mu_B$ for Al–Mn, Al–Cu–Mn and Al–Pd–Mn quasi-crystals (Fukamichi *et al* 1987, 1991, 1993, Hattori *et al* 1994). Because of the large magnetic moment of the heavy rare-earth element, the establishment of the spin-glass state is also expected for the present $Mg_{42}RE_8Zn_{50}$ quasi-crystals. Therefore, the measurement of the magnetic field cooling effect has been carried out. The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ alloys in a field of 30 Oe are displayed in figure 5. They exhibit a marked hysteresis between ZFC and FC magnetizations at low temperatures.

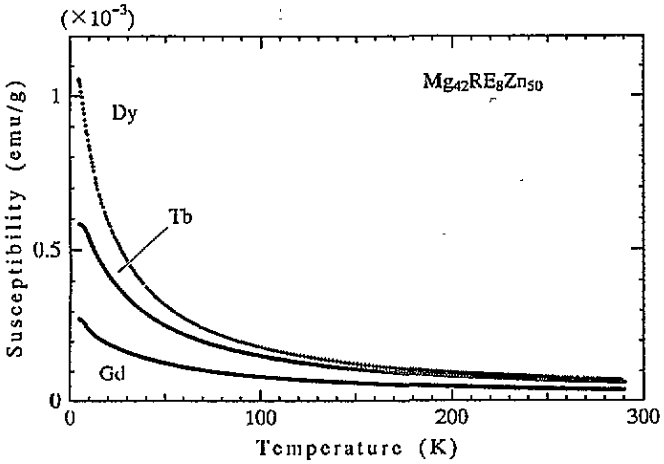

Figure 3. Temperature dependence of the DC magnetic susceptibility for the $Mg_{42}Gd_8Zn_{50}$, $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Dy_8Zn_{50}$ quasi-crystals.

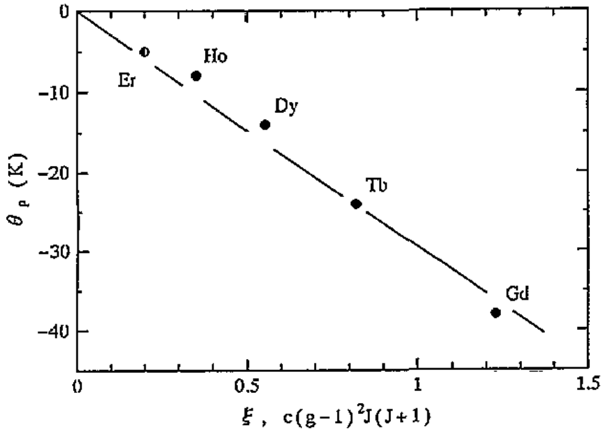

Figure 4. The paramagnetic Curie temperature Θ_p versus the de Gennes factor for the $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) quasi-crystals.

Shown in figure 6 is the temperature dependence of the AC susceptibility χ_{AC} for icosahedral $Mg_{42}Gd_8Zn_{50}$ and icosahedral $Mg_{42}Tb_8Zn_{50}$ at a frequency of 80 Hz in a field amplitude of 10 Oe. The temperature dependences of χ_{AC} exhibit a characteristic cusp to a spin glass at 5.5 K and 7.6 K, respectively. From these results, these quasi-crystals are concluded to be spin glasses. Because the spin freezing is very sensitive to the strength of the applied DC magnetic field (Fujita *et al* 1993), the cusp temperature of the ZFC magnetization in a DC magnetic field is lower than that of the AC magnetic susceptibility. The magnetization curves of the $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ are not saturated easily in the magnetic fields up to 55 kOe. The $Mg_{42}Dy_8Zn_{50}$, $Mg_{42}Ho_8Zn_{50}$ and $Mg_{42}Er_8Zn_{50}$ quasi-crystals exhibit no spin-glass behaviour above 2 K. It is known that the magnetic transition temperature is almost proportional to the de Gennes factor ξ, and its values for Gd and Tb are 15.75 and

10.50, respectively (de Gennes 1958). In these quasi-crystals, the concentrations c of the magnetic rare-earth element are the same as mentioned before. It is worth noting that the T_f of 7.6 K for $Mg_{42}Tb_8Zn_{50}$ is higher than that of 5.5 K for $Mg_{42}Gd_8Zn_{50}$ in contrast with the value of ξ. Similar behaviour has been reported for some crystalline compounds such as RE_2Zn_{17} (Stewart and Coles 1974) and REAl (Bécle *et al* 1970) compounds. For these crystalline systems, the Néel temperature T_N of RE ≡ Tb is higher than that of RE ≡ Gd.

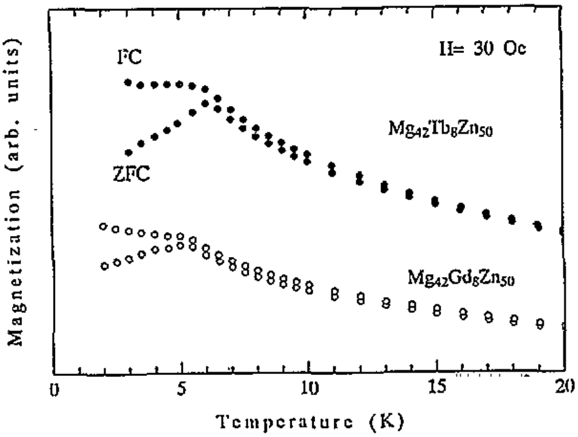

Figure 5. Temperature dependence of the ZFC and FC magnetizations for the $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasi-crystals in a field of 30 Oe.

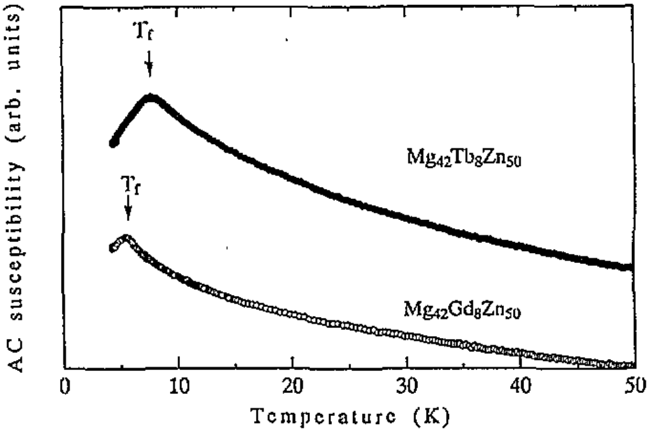

Figure 6. *Temperature dependence of the* AC *magnetic susceptibility for the* $Mg_{42}Gd_8Zn_{50}$ *and* $Mg_{42}Tb_8Zn_{50}$ quasi-crystals at 80 Hz in an AC magnetic field of 10 Oe.

For $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasi-crystals, the competition of ferromagnetic and antiferromagnetic interactions of Gd–Gd and Tb–Tb due to the exchange fluctuations is

Table 2. The effective magnetic moment $\mu_{\rm eff}$, the paramagnetic Curie temperature Θ_p and spin freezing temperature T_f for the $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) quasi-crystals.

	$\mu_{\rm eff}$ (μ_B)	RE^{3+} (μ_B)	Θ_p (K)	T_f (K)
$Mg_{42}Gd_8Zn_{50}$	7.95	7.94	−38	5.5
$Mg_{42}Tb_8Zn_{50}$	10.29	9.72	−24	7.6
$Mg_{42}Dy_8Zn_{50}$	10.83	10.64	−14	—
$Mg_{42}Ho_8Zn_{50}$	10.08	10.60	−8	—
$Mg_{42}Er_8Zn_{50}$	8.88	9.58	−5	—

considered to cause the spin-glass state. The magnetic properties of the $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) quasi-crystals are listed in table 2.

In conclusion, the quasi-crystalline phases of $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ with the highly ordered face-centred icosahedral lattice exhibit spin-glass behaviour and their spin freezing temperatures T_f are 5.5 K and 7.6 K, respectively, although the concentration of the magnetic element is lower than that of the Al-based quasi-crystalline alloys. The magnetic susceptibility of the $Mg_{42}RE_8Zn_{50}$ (RE ≡ Gd, Tb, Dy, Ho or Er) quasi-crystals show a Curie–Weiss-type temperature dependence with a negative paramagnetic Curie temperature Θ_p, indicating that the antiferromagnetic exchange interactions are predominant. Furthermore, the value of Θ_p is almost proportional to the de Gennes factor.

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