Electronic specific heat coefficient and magnetic entropy of icosahedral Mg-RE-Zn (RE=Gd, Tb and Y) quasicrystals

1995 J. Phys.: Condens. Matter 7 4183

(http://iopscience.iop.org/0953-8984/7/22/002)

J. Phys.: Condens. Matter 7 (1995) 4183–4191. Printed in the UK

Electronic specific heat coefficient and magnetic entropy of icosahedral Mg–RE–Zn (RE = Gd, Tb and Y) quasicrystals

Y Hattori†, K Fukamichi†, K Suzuki‡, A Niikura‡, A P Tsai‡, A Inoue‡ and T Masumoto‡

† Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980-77, Japan

‡ Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Received 3 January 1995, in final form 28 February 1995

Abstract. The low-temperature specific heat for non-magnetic $Mg_{42}Y_8Zn_{50}$ quasicrystal has been investigated to get information on the electronic structure. The electronic specific heat coefficient γ is estimated to be 0.63 mJ mol^{-1} K^{-2}, which is about 70% of the value expected from the free-electron model. This small γ value strongly suggests the existence of a pseudogap of the electronic density of states in the vicinity of the Fermi level.

The low-temperature specific heats of icosahedral $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasicrystals, which exhibit spin-glass behaviour, have also been investigated. The specific heat of $Mg_{42}Gd_8Zn_{50}$ exhibits a broad maximum at a temperature that is a few kelvins above the spin freezing temperature T_f determined by AC susceptibility measurements. The magnetic entropy at T_f for the $Mg_{42}Gd_8Zn_{50}$ quasicrystal reaches about 30% of the theoretical value of $R\ln 8$, being comparable to those of crystalline spin-glass systems such as magnetically dilute AuFe and CuMn alloys. The magnetic specific heat of $Mg_{42}Tb_8Zn_{50}$ quasicrystal is smaller than that of $Mg_{42}Gd_8Zn_{50}$, suggesting the splitting of the ground state due to the local electrostatic field.

1. Introduction

Recently, the formation of quasicrystals in Mg–Y–Zn and Mg–Mischmetals–Zn systems, although they contain a large amount of crystalline phases, has been reported (Luo *et al* 1993, Tang *et al* 1993). It has been confirmed that icosahedral Mg–RE–Zn (RE = Y, Tb, Dy, Ho and Er) quasicrystals are thermodynamically stable and have a highly ordered face-centred icosahedral lattice with a Frank–Kasper type of structure (Niikura *et al* 1994). Further, the quasicrystals close to the single phase have been obtained for $Mg_{42}RE_8Zn_{50}$ (RE = Y, Gd, Tb, Dy, Ho and Er) by conventional solidification, and their structural coherence length becomes 1000 Å, comparable to those of crystals (Tsai *et al* 1994).

The band calculation of the Frank–Kasper phase in the Al–Li–Cu system points out the existence of a pseudogap at the Fermi level, which contributes to stabilizing the atomic structure through the Hume-Rothery mechanism (Fujiwara and Yokokawa 1990). From the similarity of the local atomic structure between the Frank–Kasper phase and quasicrystalline counterpart, it is expected that the latter also has pseudogap at the Fermi level. In fact, the valence band structures of the thermodynamically stable quasicrystals studied by photoemission spectroscopy exhibit a minimum in the vicinity of the Fermi level E_F (Belin and Traverse 1991, Matubara *et al* 1992, Mori *et al* 1991, Mizutani *et al* 1993). A very small electronic specific heat coefficient γ relative to the free-electron value has been

0953-8984/95/224183+09$19.50

regarded as evidence of the pseudogap (Wagner *et al* 1989, Kimura *et al* 1989, Mizutani *et al* 1990). Therefore, the investigation of γ for a new thermodynamically stable quasicrystal $Mg_{42}Y_8Zn_{50}$ is of interest.

It is known that the magnetic properties are very sensitive to their local atomic structures, and hence peculiar magnetic properties are expected because of the quasicrystalline structure. From this viewpoint, the magnetic properties of $Mg_{42}RE_8Zn_{50}$ (RE = Gd, Tb, Dy, Ho and Er) quasicrystals have been investigated and the spin-glass behaviour has been observed in the icosahedral $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasicrystals (Hattori *et al* 1995b) in a similar manner to Al–Mn, Al–Cu–Mn and Al–Pd–Mn quasicrystalline alloy systems (Fukamichi *et al* 1987, 1991, 1993, Goto *et al* 1988, Matsuo *et al* 1993, Hattori *et al* 1994). The measurement of low-temperature specific heat for icosahedral $Mg_{42}RE_8Zn_{50}$ (RE = Gd and Tb) quasicrystals is very attractive because it gives information on the magnetic properties and the quasicrystal structure.

In the present paper, therefore, the electronic specific heat coefficient γ of non-magnetic $Mg_{42}Y_8Zn_{50}$ quasicrystal has been investigated and correlated with the stabilization of the atomic arrangement in the quasicrystals. Furthermore, the magnetic specific heat and the magnetic entropy at the spin freezing temperature T_f have been discussed for icosahedral $Mg_{42}RE_8Zn_{50}$ (RE = Gd and Tb) quasicrystals.

2. Experimental details

The purities of the starting materials were 99.9 wt.% pure Y, Gd and Tb and 99.99% Mg and Zn. The ingots were made by induction melting in a pyrolytic boron nitride crucible in an argon atmosphere. The $Mg_{42}Y_8Zn_{50}$ quasicrystal was susbsequently annealed at 573 K for 24 h in an evacuated quartz tube. The quasicrystalline state was confirmed by powder x-ray diffraction using Cu Kα radiation and by transmission electron microscopy (TEM). The compositional analysis was made by an inductively coupled plasma (ICP) method. The low-temperature specific heat measurements of icosahedral $Mg_{42}RE_8Zn_{50}$ (RE = Gd, Tb and Y) quasicrystals were made from 18 to 20 K by a conventional heat-pulsed method, cooling being achieved by a helium bath at 1 K via a mechanical heat switch. The thermal contact was obtained using Apiezon N grease. The bulk sample with a mass of about 2 g was fixed with nylon lines in a chamber evacuated to $\sim 10^{-7}$ Torr to keep the thermal isolation. The mass density of the sample was measured by the Archimedean method with toluene as the working fluid.

3. Results and discussion

The specific heat of non-magentic $Mg_{42}Y_8Zn_{50}$ quasicrystal has been investigated to get information on the electronic structure. Shown in figure 1 is the temperature dependence of low-temperature specific heat of the $Mg_{42}Y_8Zn_{50}$ quasicrystal, together with the fitted curve. The specific heat of many alloys and compounds can be fitted by the equation

$$C = \gamma T + \alpha T^3 + \delta T^5 \tag{1}$$

where γ is the electronic specific heat coefficient, and α and δ are the lattice specific heat coefficients. The third term represents a deviation from the Debye model. As seen from figure 1, the present data are well fitted to equation (1). The resultant values of γ, α and

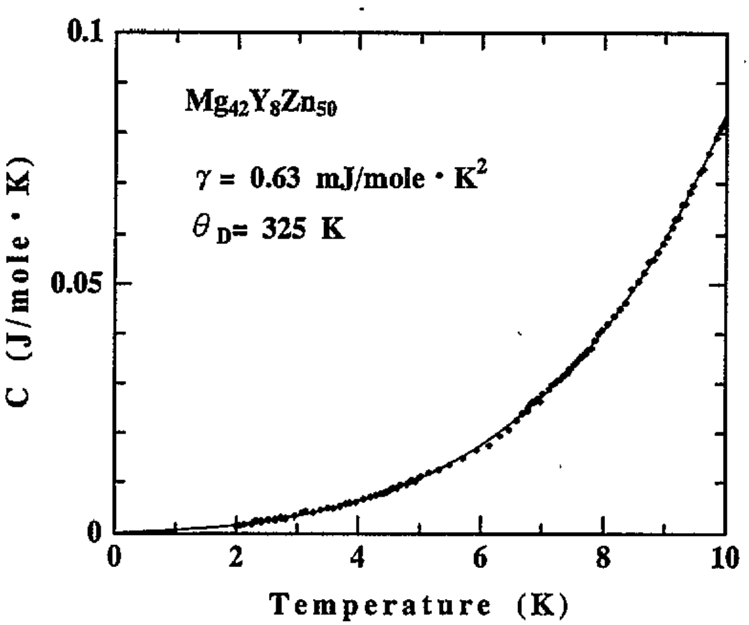

Figure 1. Temperature dependence of low-temperature specific heat for the $Mg_{42}Y_8Zn_{50}$ quasicrystal. The full curve is fitted to $C = \gamma T + \beta T^3 + \delta T^5$.

δ are 0.63 mJ mol^{-1} K^{-2}, 5.59 × 10^{-2} mJ mol^{-1} K^{-4} and 2.16 × 10^{-4} mJ mol^{-1} K^{-6}, respectively. The Debye temperature θ_D is obtained from the lattice specific heat coefficient β through the following expression:

$$\theta_D = (12\pi^4 R/5\beta)^{1/3}. \qquad (2)$$

The magnitude of θ_D for the $Mg_{42}Y_8Zn_{50}$ quasicrystal estimated to be 325 K. The present δ value is comparable to those of Mg–Al–Zn quasicrystals, which have a similar Debye temperature (Matsuda *et al* 1989).

The γ value deduced from the free-electron model can be obtained from

$$\gamma_{\text{free}} = 0.136(A/d)^{2/3}(e/a)^{1/3} \qquad (3)$$

where A is the average atomic weight (g), d the mass density (g cm^{-3}) and e/a the valence concentration. The value of e/a has been estimated to be 2.08 for icosahedral $Mg_{42}RE_8Zn_{50}$ (RE = Y, Gd, Tb, Dy, Ho and Er) quasicrystals (Tsai *et al* 1994). The value of d for the $Mg_{42}Y_8Zn_{50}$ quasicrystal measured by the Archimedean method is 4.53 g cm^{-3}. Therefore, the ratio $\gamma_{\text{exp}}/\gamma_{\text{free}}$ turns out to be about 0.7, i.e. the γ_{exp} value is less than that expected from the free-electron model. Such a small γ_{exp} strongly suggests the existence of a pseudogap near the Fermi level. The relation between the small γ value and the phase stability of icosahedral Al–Cu–Fe, Mg–Ga–Zn and Al–Li–Cu quasicrystals has been discussed in connection with the Fermi surface–Brillouin zone interaction (Wagner *et al* 1989). The formation of the pseudogap at the Fermi level reduces the energy of an electron in the vicinity of the Fermi level, leading to the stabilization of the atomic structure. The present icosahedral Mg–RE–Zn quasicrystals have been reported to be stable up to their melting point (Niikura *et al* 1994). Therefore, it is considered that the small γ value contributes to the stabilization of the atomic structure in the present quasicrystals. The ratio $\gamma_{exp}/\gamma_{free}$ as a function of the valence concentration e/a for some Frank–Kasper type quasicrystals of sp-electron systems such as Mg–Zn–Ga (Mizutani *et al* 1990, 1991), Mg–Al–Cu, Mg–Al–Ag (Mizutani *et al* 1990) and Al–Li–Cu (Kimura *et al* 1989) has been discussed, and it has been pointed out that $\gamma_{exp}/\gamma_{free}$ becomes smaller with decreasing e/a regardless of the alloy system (Mizutani *et al* 1991). A large peak due to d states of Cu and Pd is located around 4 eV for Al–Cu–Fe (Mori *et al* 1991) and Mg–Al–Pd (Hashimoto *et al* 1994) quasicrystals. The formation of covalent bonding between the 3p electrons of Al and the 4d electron of Pd contributes to the reduction of 3p electrons in the vicinity of the Fermi level E_F, resulting in high resistivity for Mg–Al–Pd quasicrystals (Hashimoto *et al* 1994). Low-temperature specific heat data for the Frank–Kasper type quasicrystals are listed in table 1. The present $\gamma_{exp}/\gamma_{free}$ of the $Mg_{42}Y_8Zn_{50}$ is much lower than that of the Mg–Ga–Zn, which have higher e/a value. However, 0.7 is larger than 0.39 for Al–Li–Cu with similar value of e/a (Kimura *et al* 1989). Note that the $Mg_{42}Y_8Zn_{50}$ possesses 4d electrons of Y, which would contribute such a slightly high density of states at the Fermi level, compared with that of simple sp-electron systems. The band calculation and the photoemission spectroscopy of this system are highly expected to be discussed in more detail.

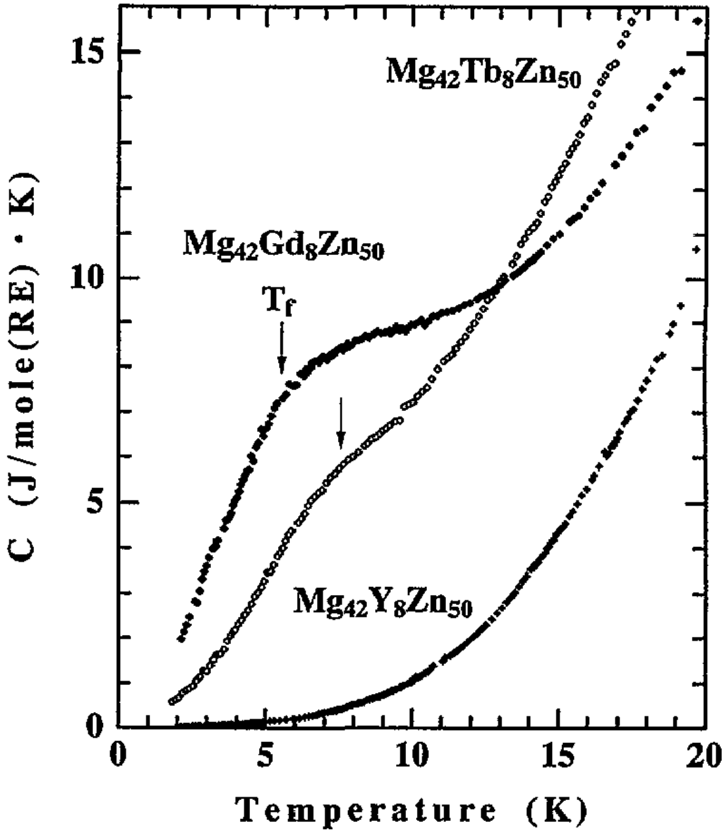

Figure 2. Temperature dependence of low-temperature specific heat for the icosahedral $Mg_{42}RE_8Zn_{50}$ (RE = Gd, Tb and Y) quasicrystals. The arrows indicate the spin freezing temperature T_f determined by the AC magnetic susceptibility measurement (Hattori *et al* 1995b).

The magnetic properties of icosahedral $Mg_{42}RE_8Zn_{50}$ (RE = Gd, Tb, Dy, Ho and Er) quasicrystals have been reported. The paramagnetic Curie temperature θ_p of the $Mg_{42}RE_8Zn_{50}$ quasicrystals is negative, showing that the RE–RE exchange interactions are predominantly antiferromagnetic. Moreover, spin-glass behaviour for the $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasicrystals has been observed below 5.5 K and 7.6 K, respectively (Hattori *et al* 1995b). In the present study, to elucidate the magnetic entropy at the spin freezing temperature T_f, the low-temperature specific heat of the $Mg_{42}Gd_8Zn_{50}$ and $Mg_{42}Tb_8Zn_{50}$ quasicrystals (which exhibit spin-glass behaviour) has been investigated. Figure 2 displays the temperature dependence of low-temperature specific heat for $Mg_{42}RE_8Zn_{50}$ (RE = Gd, Tb and Y) quasicrystals. The arrow indicates the spin freezing temperature determined by the AC magnetic susceptibility measurement (Hattori *et al* 1995b). As seen in the figure, the specific heat curve of $Mg_{42}Gd_8Zn_{50}$ quasicrystal exhibits a broad maximum at a temperature that is higher than the spin freezing temperature T_f. The magnetic contribution to the specific heat for the $Mg_{42}Tb_8Zn_{50}$ quasicrystal seems to be smaller than that for the $Mg_{42}Gd_8Zn_{50}$ quasicrystal, although the total angular momentum of Tb^{3+} ($J = 6$) is larger than that of Gd^{3+} ($J = 7/2$). The magnetic contribution to the specific heat has been separated for discussion in more detail. Assuming that the lattice and electronic specific heats of $Mg_{42}Y_8Zn_{50}$ are the same as those of $Mg_{42}Gd_8Zn_{50}$, the magnetic specific heat of the latter can be obtained as the difference in the specific heat between them. The Debye temperature θ_D of pure Y and Gd is about 280 and 200 K, respectively. However, the present quasicrystals contain only about 8 at.% of RE element. Therefore, the assumption mentioned above is reasonable. The magnetic contribution to the specific heat of the $Mg_{42}Gd_8Zn_{50}$ quasicrystal exhibits a broad maximum at a temperature that is about 3 K higher than T_f as shown in figure 3. This behaviour is very similar to other spin-glass systems such as a crystalline CuMn magnetically dilute alloy (Wenger and Keesom 1976) and $Eu_xSr_{1-x}S$ ($x = 0.40$ and 0.54) compounds (Meschede *et al* 1980). Namely, the temperature at which the specific heat reaches a maximum is higher than T_f. As seen from the figure, the magnetic contribution does not vanish even above 30 K, being accompanied by a long tail.

The magnetic entropy S_{mag} is given by the following equation:

$$S_{mag} = \int_0^{T_M} \frac{C_{mag}}{T} dT \tag{4}$$

where T_M is the long-range magnetic ordering temperature, and C_{mag} the magnetic contribution to the specific heat. In the case of long-range magnetic order transition, S_{mag} is nearly equal to $R\ln(2J+1)$, where R is the gas constant and J is the angular momentum quantum number. On the other hand, the development of S_{mag} at T_f for the crystalline AuFe and CuMn magnetically dilute alloys becomes 22–30% of the theoretical values, which is much smaller than those of the long-range ferromagnetic and antiferromagnetic ordering temperature (Wenger and Keesom 1976). The inset in figure 3 is the temperature dependence of magnetic entropy S_{mag} for the $Mg_{42}Gd_8Zn_{50}$ quasicrystal obtained from equation (4). The value of S_{mag} reaches about 30% of the theoretical value of $R\ln 8$, being comparable to those of other crystalline spin-glass systems. On the other hand, it is noteworthy that S_{mag} at T_f for amorphous Er–Ni random magnetic anisotropy system is 45–60% of $R\ln(2J+1)$ (Hattori *et al* 1995a).

Figure 4 displays the temperature dependence of the difference in the specific heat between $Mg_{42}RE_8Zn_{50}$ (RE = Gd and Tb) and non-magnetic $Mg_{42}Y_8Zn_{50}$ in the form of C/T versus T^2. Compared with $Mg_{42}Gd_8Zn_{50}$, the specific heat of $Mg_{42}Tb_8Zn_{50}$ gradually decreases with decreasing temperature, and indicates the occurrence of the Schottky-type

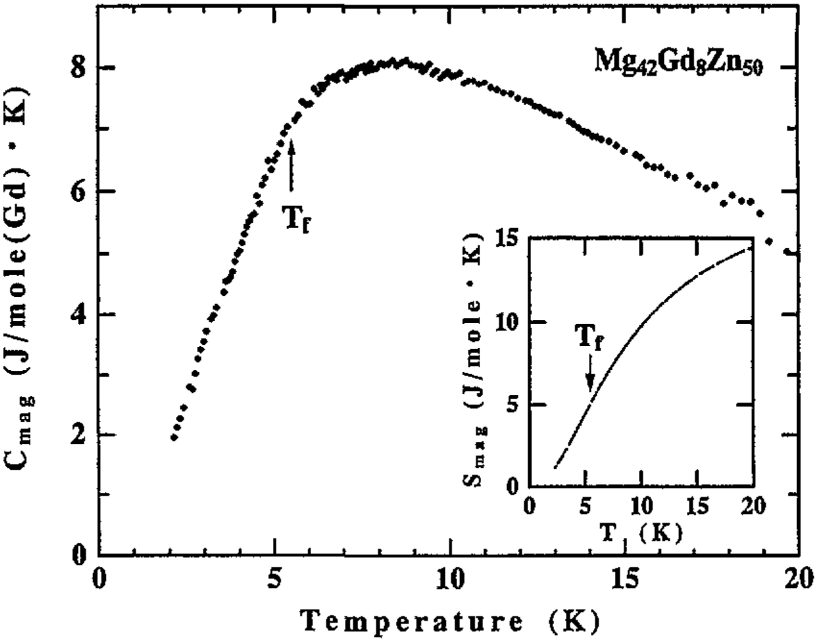

Figure 3. Temperature dependence of the magnetic contribution to the specific heat for $Mg_{42}Gd_8Zn_{50}$ quasicrystal. The inset exhibits the temperature dependence of the magnetic entropy. The arrows indicate the spin freezing temperature T_f determined by the AC magnetic susceptibility measurement (Hattori *et al* 1995b).

specific heat $C_{Schottky}$. That is, the degeneracy of Tb ion is considered to split due to the electrostatic field, which acts on the orbital angular momentum, and the magnetic specific heat becomes smaller in spite of the larger total angular momentum of Tb ion. We cannot separate exactly C_{mag} from the total specific heat because of the lack of information on $C_{Schottky}$. Shown in figure 5 is the temperature dependence of the difference in total entropy for the $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Y_8Zn_{50}$ quasicrystals. The difference in the total entropy is considered to give the sum of the Schottky-type and the magnetic entropy ($S_{mag} + S_{Schottky}$). The value of ($S_{mag} + S_{Schottky}$) at T_f is about 3.6 J (mol Tb)$^{-1}$ K^{-2}. At the present stage, by assuming that the development of S_{mag} for $Mg_{42}Tb_8Zn_{50}$ is about 30% of $R\ln(2J+1)$, the degeneracy $(2J+1)$ should be 2 or 3 because 3.6 J (mol Tb)$^{-1}$ K^{-2} is equal to 31% of $R\ln 4$. That is, if $(2J+1)$ is 4, $S_{Schottky}$ diminishes completely. Therefore, the ground state of Tb should be a doublet or triplet, implying the low symmetry of Tb site in the quasicrystal. The structural analysis of a single-grained Mg–Y–Zn quasicrystal indicates that the Y atom does not occupy the centre of the icosahedral cluster (Yamamoto *et al* 1994). Taking the similarity of structure for the $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Y_8Zn_{50}$ quasicrystals into consideration, the small degeneracy of Tb ion is consistent with the result of the structural analysis.

In conclusion, the electronic specific heat coefficient γ of the $Mg_{42}Y_8Zn_{50}$ quasicrystal is about 0.63 mJ mol^{-1} K^{-2}, indicating a very low density of states at the Fermi level. Further, the γ value is small relative to that of free electrons. These results strongly suggest the existence of a pseudogap of the electronic density of states in the vicinity of the Fermi level. The specific heat of the icosahedral $Mg_{42}Gd_8Zn_{50}$ quasicrystal shows a broad maximum at a temperature a few kelvins higher than the spin freezing temperature T_f. The

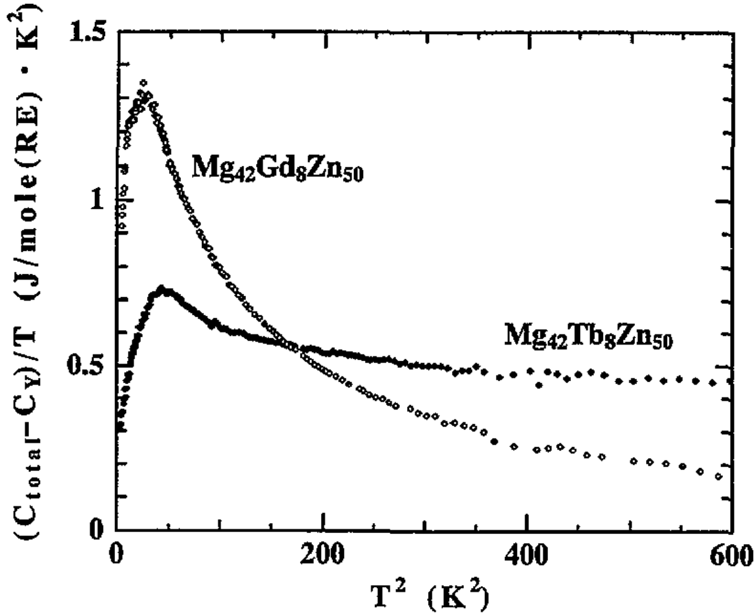

Figure 4. Temperature dependence of the difference in the total specific heat between magnetic $Mg_{42}RE_8Zn_{50}$ (RE = Gd and Tb) quasicrystals and non-magnetic $Mg_{42}Y_8Zn_{50}$ quasicrystal in the form of C/T versus T^2.

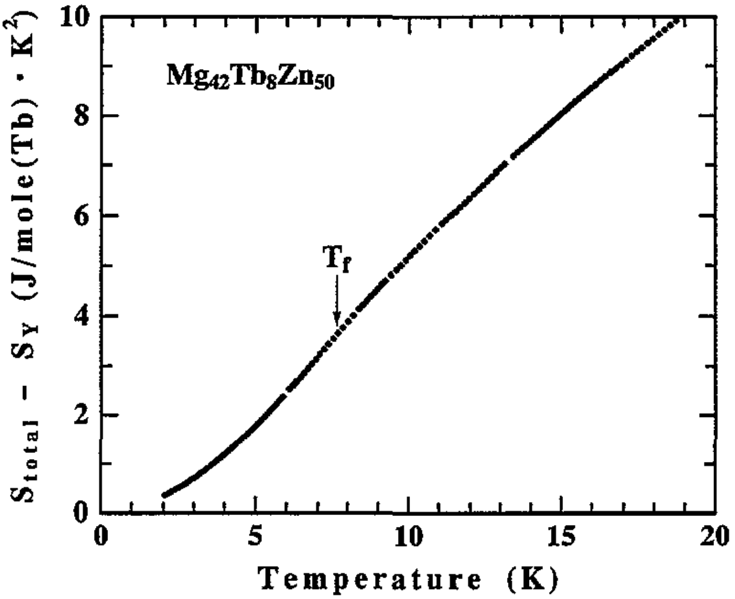

Figure 5. Temperature dependence of the difference in the total entropy between $Mg_{42}Tb_8Zn_{50}$ and $Mg_{42}Y_8Zn_{50}$ quasicrystals.

magnetic entropy at T_f reaches about 30% of the value of $R \ln 8$ for the long-range magnetic order transition. These two results are very similar to other crystalline spin-glass systems. The magnetic specific heat of $Mg_{42}Tb_8Zn_{50}$ is much smaller than that of $Mg_{42}Gd_8Zn_{50}$, showing the splitting of the ground state due to the local electrostatic field, which acts on the 4f moment of Tb ion. The ground state of Tb ion is considered to be a Kramers doublet or triplet, suggesting the low symmetry of Tb site in the quasicrystal structure.

Table 1. Low-temperature specific heat data for Frank–Kasper type quasicrystals.

	γ_{exp} (mJ mol^{-1} K^{-2})	$\gamma_{exp}/\gamma_{free}$	e/a	θ_D (K)
$Mg_{42}Y_8Zn_{50}$	0.63	0.7	2.08	325
$Al_{55}Li_{35.8}Cu_{9.2}$[a]	0.318	0.39	2.09	341
$Mg_{33.5}Zn_{40}Ga_{26.5}$[b]	0.91	1.05	2.265	353

[a] Kimura *et al* (1989).

[b] Mizutani *et al* (1990).

Acknowledgments

The support by a Grant-in-Aid for Developmental Scientific Research (B)(2), 05555178, from the Japanese Ministry of Education, Science and Culture, is appreciated. The authors would like to thank Mr S Terashima for his assistance in the low-temperature specific heat measurements.

References

Belin E and Traverse A 1991 *J. Phys.: Condens. Matter* **3** 2157–66
Fujiwara T and Yokokawa T 1990 *Quasicrystals (Springer Ser. Solid State Sci 93)* (Berlin: Springer) pp 196–204
Fukamichi K, Goto T, Masumoto T, Sakakibara T, Oguchi M and Todo S 1987 *J. Phys. F: Met. Phys.* **17** 743–52
Fukamichi K, Hattori Y, Nakane and Goto T 1993 *Mater. Trans. JIM* **34** 122–7
Fukamichi K, Kikuchi T, Hattori Y, Tsai A P, Inoue A and Masumoto T 1991 *Proc. China–Japan Seminars on quasicrystals (Beijing, November 1990)* (Singapore: World Scientific)
Goto T, Sakakibara T and Fukamichi K 1988 *J. Phys. Soc. Japan* **57** 1751–7
Hashimoto K, Yamada Y, Yamauchi T, Tanaka T, Matsuda T and Mizutani U 1994 *Mater. Sci. Eng.* A **181–2** 785–9
Hattori Y, Fukamichi K, Chikama H, Katori-Aruga H and Goto T 1994 *J. Phys.: Condens. Matter* **6** 10129–40
Hattori Y, Fukamichi K, Suzuki K, Katori-Aruga H and Goto T 1995a *J. Phys.: Condens. Matter* at press
Hattori Y, Niikura A, Tsai A P, Inoue A, Masumoto T, Fukamichi K, Katori-Aruga H and Goto T 1995b *J. Phys.: Condens. Matter* **7** 2313
Kimura K, Iwahashi H, Hashimoto T, Takeuchi S, Mizutani U, Ohashi S and Itoh G 1989 *J. Phys. Soc. Japan* **58** 2472–81
Luo Z, Zhang S, Tang Y and Zhao D 1993 *Scr. Metall.* **28** 1513–18
Matsuda T, Ohara I, Sato H, Ohashi S and Mizutani U 1989 *J. Phys.: Condens. Matter* **1** 4087–98
Matsuo S, Nakano H, Ishimasa T and Mori M 1993 *J. Phys. Soc. Japan* **62** 4044–52
Matubara H, Ogawa S, Kinoshita T, Kishi K, Takeuchi S, Kimura K and Suga S 1991 *Japan. J. Appl. Phys.* **30** L389–92
Meschede D, Steglich F, Felsch W, Maletta H and Zinn W 1980 *Phys. Rev. Lett.* **44** 102–5
Mizutani U, Kamiya A, Matsuda T, Kishi K and Takeuchi S 1991 *J. Phys.: Condens. Matter* **3** 3711–18
Mizutani U *et al* 1993 *J. Non-Cryst. Solids* **156–8** 882–6
Mizutani U, Sakabe Y, Shibuya T, Kishi K, Kimura K and Takeuchi S 1990 *J. Phys.: Condens. Matter* **2** 6169–78

Mori M, Matsuo S, Ishimasa T, Matsuura T, Kamiya K, Inokuchi H and Matsukawa T 1991 *J. Phys.: Condens. Matter* **3** 767–71

Niikura A, Tsai A P, Inoue A and Masumoto T 1994 *Phil. Mag. Lett.* **69** 351–5

Tang Y L, Zhao D S, Luo Z P, Shen N F and Zhang S Q 1993 *Scr. Metall.* **29** 955–8

Tsai A P, Niikura A, Inoue A, Masumoto T, Nishida Y, Tsuda K and Tanaka M 1994 *Phil. Mag. Lett.* **70** 169–75

Wagner J L, Wong K M and Poon S J 1989 *Phys. Rev.* **39** 8091–5

Wenger L E and Keesom P H 1976 *Phys. Rev.* B **13** 4053–9

Yamamoto Y, Weber S, Ohshima K, Niikura A, Tsai A P, Inoue A and Masumoto T 1994 private communication