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Electronic specific heat measurements for quasicrystals and Frank–Kasper crystals in Mg–Al–Ag, Mg–Al–Cu, Mg–Al–Zn, Mg–Ga–Zn and Al–Li–Cu alloy systems

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Abstract. The electronic specific heat coefficient was measured for sp electron quasicrystals and the corresponding Frank–Kasper crystals in Mg–Al–Ag, Mg–Al–Cu, Mg–Al–Zn, Mg–Ga–Zn and Al–Li–Cu alloy systems. It turned out that the ratio $\gamma_{\text{exp}}/\gamma_{\text{F}}$ plotted against the average number of electrons per atom is essentially identical between the quasicrystalline and Frank–Kasper phases: it decreases with decreasing electron concentration per atom, e/a , and is extrapolated to zero at about $e/a = 2.0$. A unique e/a dependence of the $\gamma_{\text{exp}}/\gamma_{\text{F}}$ in the Frank–Kasper phase is discussed in terms of the Fermi surface–Brillouin zone interaction specific to this structure. Judging from the identical e/a dependence of $\gamma_{\text{exp}}/\gamma_{\text{F}}$, we conclude that a similar Fermi surface–Brillouin zone interaction ought to be essential in determining the density of states at the Fermi level in the quasicrystalline phase. The electronic structure near the Fermi level is essentially determined by the local atomic structure, which happens to be similar between these two intriguing phases.

1. Introduction

The icosahedral quasicrystals in the Mg–Al–Ag [1, 2], Mg–Al–Cu [2, 3] and Mg–Al–Zn [4] alloy systems can be obtained as metastable states by rapid quenching from the melt. The valence-band structure in these quasicrystals is dominated by the sp electrons at the Fermi level. Hence they are often called sp-electron quasicrystals. Upon heating, some of them are known to crystallize into the Frank–Kasper phase [5], which possesses the same icosahedral symmetry as the quasicrystal at each lattice site in a large BCC unit cell. The Frank–Kasper phase also exists in the Mg–Ga–Zn [6] and Al–Li–Cu [7] alloy systems, both of which are again typical of the sp-electron system. It was found that the $\text{Mg}_{39.5}\text{Ga}_{20.5}\text{Zn}_{40}$ quasicrystal obtained by rapid quenching is stable up to almost the melting point without crystallization [2]. Hence, the composition range, where the Frank–Kasper phase is formed in the Mg–Ga–Zn system, differs from the range over which the stable quasicrystal mentioned above can be obtained. A similar situation exists in the Al–Li–Cu system, since the thermodynamically stable quasicrystal, often referred to as the T2 phase, competes with the Frank–Kasper phase or so called R phase. Hence,

in spite of the common feature characterized by the possession of the icosahedral symmetry, the location in the composition diagram and the stability of the quasicrystal relative to the corresponding Frank–Kasper phase are subtly different from system to system.

Kimura *et al* [8] recently reported that the thermodynamically stable $\text{Al}_{55.0}\text{Li}_{35.8}\text{Cu}_{9.2}$ quasicrystal possesses a very small electronic specific heat coefficient, $\gamma_{\text{exp}} = 0.318 \text{ mJ mol}^{-1} \text{ K}^{-2}$, which is merely one third of the corresponding free electron value. This indicates the presence of a deep minimum in the density of states at the Fermi level. Fujiwara and Yokokawa [9] have calculated the band structure for the Frank–Kasper phase in the Al–Li–Cu system and have pointed out that the pseudogap opens at the Fermi level because of strong Bragg scattering. Judging from the similarity in the local atomic arrangements for both quasicrystalline and Frank–Kasper phases, one may presume that the quasicrystalline phase also possesses a similar pseudogap at the Fermi level and that the observed small value of γ_{exp} in the quasicrystalline phase is merely its reflection.

The data for the electronic specific heat coefficient for the sp-electron quasicrystals have been accumulated in the last few years [2, 4, 8, 10]. However, the available data on the Frank–Kasper crystalline phase are still limited [4, 11]. Since realistic band calculations have been made so far for the crystalline phase, it is important to accumulate more data for the Frank–Kasper phase and to compare systematically the electronic specific heat coefficient in both quasicrystal and the corresponding Frank–Kasper phase in as many alloy systems as possible. The present studies are intended to supplement the previously reported data [2, 4] through measurements of the low temperature specific heats, particularly for the Frank–Kasper phase in the above alloy systems.

2. Experimental procedure

Alloy systems studied in this experiment included Mg–Al–Ag, Mg–Al–Cu, Mg–Al–Zn, Mg–Ga–Zn and Al–Li–Cu. All Mg-based alloy ingots were obtained by induction-melting appropriate amounts of constituent elements 99.95% Mg, 99.999% Al, 99.999% Ag, 99.999% Cu, 99.999% Zn and 99.999% Ga in a high-purity graphite crucible under a pressurized He atmosphere. In the first three alloy systems Mg–Al–Ag, Mg–Al–Cu and Mg–Al–Zn, the following alloy compositions were chosen with the aim of obtaining the quasicrystal and/or the Frank–Kasper phase: $\text{Mg}_{36.4}\text{Al}_{54.5}\text{Ag}_{9.1}$, $\text{Mg}_{39.5}\text{Al}_{51.9}\text{Cu}_{8.6}$, $\text{Mg}_{39.5}\text{Al}_{35.3}\text{Cu}_{25.2}$, $\text{Mg}_{39.5}\text{Al}_{30.25}\text{Cu}_{30.25}$ and $\text{Mg}_{39.3}\text{Al}_{21.4}\text{Zn}_{39.3}$. On the other hand, Mg_2GaZn_3 or $\text{Mg}_{33.3}\text{Ga}_{16.7}\text{Zn}_{50.0}$ was chosen in the Mg–Ga–Zn system, since the Frank–Kasper phase was reported to form at this composition [6].

Firstly, ribbon specimens were fabricated using a single-roll spinning wheel apparatus operated in a reduced Ar gas atmosphere. The formation of the quasicrystalline phase was checked by ordinary x-ray diffraction with $\text{CuK}\alpha$ radiation. The crystallization into the Frank–Kasper phase has been monitored by measuring the differential scanning calorimetry (DSC) spectrum with a heating speed of 20 K min^{-1} . All Mg-based quasicrystals were transformed into the Frank–Kasper phase by annealing at 650 K for 1 h in vacuum.

The Frank–Kasper crystal was also prepared in the Al–Li–Cu alloy system. The preparation was the same as that for the thermodynamically stable quasicrystal in this system [8]. Briefly, the Al–Li–Cu ingot was prepared by adding 99.9% Li to the molten Al–Cu alloy covered with LiCl flux in an alumina crucible. The ingot sealed in the BN

crucible under vacuum was remelted in the Bridgman furnace. A large grained sample was grown at 800 °C for a week. The FCC Al second phase was removed by chemical etching.

The low-temperature specific heat was measured in the temperature range 1.5–6 K, using the DC adiabatic method. Since both the Frank–Kasper crystals and the quasicrystals were brittle, each sample of 1–1.5 g in weight was crushed into powder and compacted into a Au-plated Cu container. The specific heat of the container was independently measured and subtracted from the total. All the data were well fitted to the ordinary equation $C = \gamma T + \alpha T^3 + \delta T^5$, where γ is the electronic specific heat coefficient, α and δ are the lattice specific heat coefficients. The Debye temperature θ_D is deduced from α through equation $\theta_D = (12\pi^4 R/5\alpha)^{1/3}$, where R is the gas constant.

3. Results and discussion

The quasicrystalline single phase has been formed by rapid quenching from the melt in the $\text{Mg}_{36.4}\text{Al}_{54.5}\text{Ag}_{9.1}$, $\text{Mg}_{39.5}\text{Al}_{51.9}\text{Cu}_{8.6}$ and $\text{Mg}_{39.3}\text{Al}_{21.4}\text{Zn}_{39.3}$ alloys. However, neither the quasicrystalline phase nor the Frank–Kasper phase has been formed in both the rapidly quenched and the annealed states in the remaining two alloys $\text{Mg}_{39.5}\text{Al}_{35.3}\text{Cu}_{25.2}$ and $\text{Mg}_{39.5}\text{Al}_{30.25}\text{Cu}_{30.25}$, although the compositions were chosen so as to conform with the general formula $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$ described in [5]. Note here that these two alloys were intentionally made to reduce the electron concentration per atom e/a to 2.1 and 2.0, respectively. Hence, it seems that the electron concentration might be too low to allow the formation of the Frank–Kasper phase in the Mg–Al–Cu system.

Figure 1 shows the x-ray diffraction spectra for the rapidly quenched $\text{Mg}_{33.3}\text{Ga}_{16.7}\text{Zn}_{50.0}$ alloy subjected to heat treatment in the DSC cell up to temperatures marked as A and B. It can be seen that, in the as-quenched state, there exist a few sharp lines in addition to a set of relatively broad lines, which can be indexed as the quasicrystal. Admittedly, the quasicrystallinity in this particular sample was rather poor, as compared with those reported in the previous studies [2]. As can be seen from the figure, the extra diffraction lines grow with increasing temperature up to 550 K but have substantially reduced intensities once the DSC spectrum exhibits an exothermic peak at about 570 K. All diffraction lines for the sample heated up to 650 K can be identified as being characteristic of the Frank–Kasper phase.

All Mg-based quasicrystals mentioned above, including the $\text{Mg}_{33.3}\text{Ga}_{16.7}\text{Zn}_{50.0}$, exhibited an exothermic peak at about 570 K in the DSC runs. The x-ray diffraction spectra after the exothermic peak can be indexed in terms of the Frank–Kasper single phase. The present results are plotted in the composition diagram in figure 2 along with the previously reported data [2, 4]. It is seen that the quasicrystalline single phase occasionally crystallizes into a mixture of the Frank–Kasper phase and unknown crystalline phases. It is not clear if this is due to the phase separation from a quasicrystal or to invisible crystallites already present in the matrix of a quasicrystal in the melt-spun sample. In general, however, we can say that the region in which the quasicrystalline single phase is found agrees with that in which the Frank–Kasper single phase is found in Mg–Al–Ag, Mg–Al–Cu and Mg–Al–Zn systems but not in the Mg–Ga–Zn and Al–Li–Cu systems.

The measured electronic specific heat coefficient is normalized with respect to the corresponding free electron value in units of $\text{mJ mol}^{-1} \text{K}^{-2}$:

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

where A is the average atomic weight in g and d is the density in g cm^{-3} . The value of

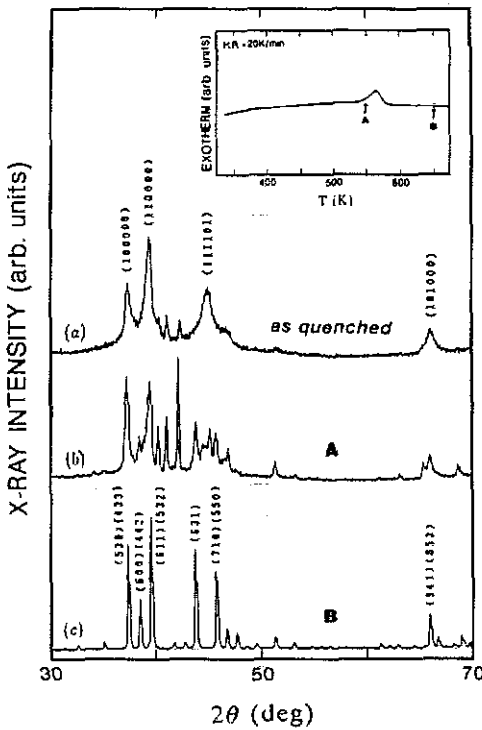


Figure 1. X-ray diffraction patterns for the Mg_2GaZn_3 or $\text{Mg}_{33.3}\text{Ga}_{16.7}\text{Zn}_{50.0}$ sample; (a) in the as-quenched state, (b) that heated up to the temperature marked as A in the DSC run shown in the inset, and (c) that heated up to the temperature marked as B. An exothermic peak in the DSC spectrum is due to the crystallization into the Frank-Kasper phase.

e/a is assigned by assuming that Ag, Cu, Li, Mg, Zn, Al and Ga donate 1, 1, 1, 2, 2, 3 and 3 electrons per atom, respectively. Numerical data are summarized in table 1.

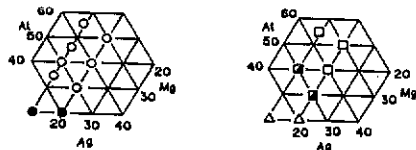
A dimensionless ratio $\gamma_{\text{exp}}/\gamma_{\text{free}}$ is plotted in figures 3 and 4 as a function of the average e/a value for the quasicrystalline phase and the Frank-Kasper phase, respectively. Several interesting features can be observed. First of all, the value of $\gamma_{\text{exp}}/\gamma_{\text{free}}$ in the quasicrystal agrees with that for the corresponding Frank-Kasper phase, within the accuracy, in all alloy systems without exception. This strongly indicates that the electronic structure, particularly near the Fermi level, in the Frank-Kasper phase is quite similar to that in the corresponding quasicrystal. As a result, the e/a dependence of the ratio becomes essentially the same between these two intriguing phases.

It can be also seen from figures 3 and 4 that the ratio decreases steeply with decreasing e/a and that it tends to become zero as e/a approaches the value of 2.0. The large Brillouin zone or the Jones zone for the Frank-Kasper phase can be constructed using as a guide the structure factor deduced from x-ray diffraction data and the fact that the Frank-Kasper phase corresponds to a $(1/1-1/1-1/1)$ rational approximant of the icosahedral phase†. One can then easily manipulate the volume of the zone and also the number of electrons per atom accommodated in the respective zones. It turned out that

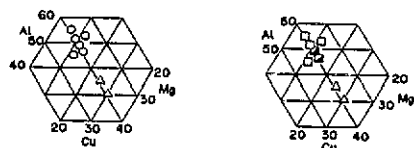
† K Edagawa, the University of Tokyo, informed us that there exists a one-to-one correspondence in the x-ray diffraction lines between the icosahedral quasicrystalline phase and the Frank-Kasper approximant phase. The details are as yet unpublished.

(A) As quenched state (B) Equilibrium state

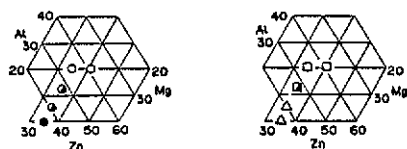
(1) Mg-Al-Ag



(2) Mg-Al-Cu



(3) Mg-Al-Zn



(4) Mg-Ga-Zn

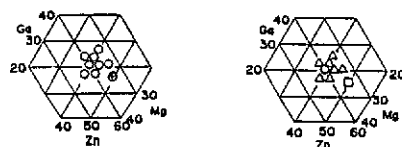


Figure 2. Composition diagrams for Mg-Al-Ag, Mg-Al-Cu, Mg-Al-Zn and Mg-Ga-Zn alloy systems: (A) as-quenched state from liquid, and (B) an equilibrium state obtained after annealing the as-quenched sample. Symbols are as follows: O: quasicrystalline single phase, □: Frank-Kasper single phase, ●: amorphous single phase, Δ: unidentified crystalline phase, ⊙: quasicrystalline phase + amorphous phase, ◩: Frank-Kasper phase + crystalline phase, ⊕: quasicrystalline phase + crystalline phase. The data in [2, 4] are incorporated.

the volumes of the zones bounded by 24 (532) + 6 (600) planes, 12 (503) planes and 24 (631) planes are $(2038/15)(2\pi/a)^3$, $(34391/250)(2\pi/a)^3$ and $(97336/495)(2\pi/a)^3$ and can accommodate 1.677, 1.698 and 2.428 electrons per atom, respectively. Here, a is the lattice constant. These electron concentrations show no immediate correspondence with $e/a = 2.0$, at which the electronic specific heat coefficient apparently diminishes in the Frank-Kasper phase. Nevertheless, we believe that the strong e/a dependence of the measured electronic specific heat coefficient is caused by the Fermi surface-Brillouin zone effects due mainly to the (503), (532) and (600) planes.

As is seen from figure 1, the major diffraction lines (100000), (110000) and (111101) in the quasicrystalline phase roughly coincide in position with the (503), (532) and (631) lines in the Frank-Kasper phase. Indeed, it can be shown† that the (100000), (110000)

† K Edagawa, the University of Tokyo, informed us that there exists a one-to-one correspondence in the x-ray diffraction lines between the icosahedral quasicrystalline phase and the Frank-Kasper approximant phase. The details are as yet unpublished.

Table 1. Low-temperature specific heat data for various quasicrystals and Frank-Kasper crystals. Q and F stand for the quasicrystalline and Frank-Kasper phases, respectively. Q + C indicates the existence of a crystalline phase in the quasicrystalline matrix. The composition of the quasicrystalline phase is listed in %, while that of the Frank-Kasper phase except for Al-Li-Cu is given in terms of the atomic ratio.

	γ $\text{mJ mol}^{-1} \text{K}^{-2}$	α $\times 10^{-2} \text{mJ mol}^{-1} \text{K}^{-4}$	δ $\times 10^{-4} \text{mJ mol}^{-1} \text{K}^{-6}$	θ_D K	γ_F $\text{mJ mol}^{-1} \text{K}^{-2}$	$\gamma_{\text{exp}}/\gamma_F$	e/a
$\text{Mg}_{55}\text{Al}_{54.5}\text{Ag}_{9.1}$	Q	1.19 ± 0.01	4.5 ± 0.2	2.3 ± 0.6	350 ± 4	0.933	1.28
$\text{Mg}_2\text{Al}_6\text{Ag}$	F	1.16 ± 0.01	3.1 ± 0.2	5.0 ± 0.7	395 ± 9	0.933	1.24
$\text{Mg}_{59}\text{Al}_{51.9}\text{Cu}_{16.6}$	Q	1.38 ± 0.01	2.7 ± 0.2	5.2 ± 0.6	414 ± 8	0.924	1.49
$\text{Mg}_{57}\text{Al}_{42}\text{Cu}_7$	F	1.40 ± 0.01	2.5 ± 0.2	4.4 ± 0.7	430 ± 10	0.924	1.51
$\text{Mg}_{55.8}\text{Al}_{51.9}\text{Cu}_{12.3}^\dagger$	Q	1.15 ± 0.01	3.2 ± 0.1	-0.6 ± 0.4	393 ± 4	0.902	1.28
$\text{Mg}_{58}\text{Al}_{42}\text{Cu}_{10}$	F	1.19 ± 0.01	2.0 ± 0.1	2.5 ± 0.5	460 ± 10	0.902	1.33
$\text{Mg}_{59.3}\text{Al}_{51.4}\text{Zn}_{9.3}$	Q	0.96 ± 0.01	3.2 ± 0.2	5.1 ± 0.6	392 ± 7	0.866	1.11
$\text{Mg}_{11}\text{Al}_6\text{Zn}_{11}$	F	1.00 ± 0.01	3.8 ± 0.2	2.4 ± 0.6	371 ± 6	0.866	1.16
$\text{Mg}_{53.3}\text{Ga}_{16.7}\text{Zn}_{50.0}$	Q + C	0.74 ± 0.01	5.8 ± 0.2	9.6 ± 0.6	323 ± 4	0.843	0.88
Mg_2GaZn_3	F	0.73 ± 0.01	5.6 ± 0.1	5.6 ± 0.4	326 ± 3	0.843	0.87
$\text{Al}_{55.0}\text{Li}_{55.8}\text{Cu}_{9.2}^\ddagger$	Q	0.318	4.19	-2.43	341	0.78	0.39
$\text{Al}_{54.6}\text{Li}_{54.0}\text{Cu}_{11.4}$	F	0.35 ± 0.01	3.2 ± 0.1	-4.0 ± 0.1	394 ± 4	0.815	0.42

[†] Reproduced from [2].

[‡] Reproduced from [8].

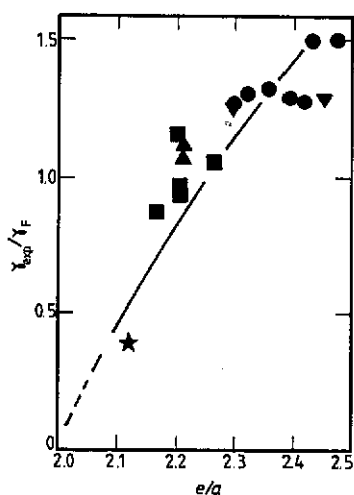


Figure 3. The ratio γ_{exp}/γ_F of the electronic specific heat coefficient over the corresponding free electron value as a function of the electrons per atom, e/a , in various quasicrystals. Symbols are as follows: ∇ : Mg-Al-Ag, \bullet : Mg-Al-Cu, \blacktriangle : Mg-Al-Zn, \blacksquare : Mg-Ga-Zn and \star : Al-Li-Cu. The data in [2, 4, 8] are incorporated.

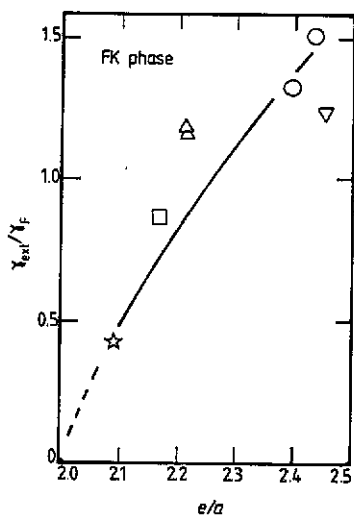


Figure 4. The ratio γ_{exp}/γ_F of the electronic specific heat coefficient over the corresponding free electron value as a function of the electrons per atom, e/a , in various Frank-Kasper crystals. Symbols are as follows: ∇ : Mg-Al-Ag, \circ : Mg-Al-Cu, \triangle : Mg-Al-Zn, \square : Mg-Ga-Zn and \star : Al-Li-Cu.

and (111101) planes split into 12 (503), 24 (532) + 6 (600) and 24 (543) + 24 (631) + 12 (710) planes, respectively, when the projection of six-dimensional hypercubic lattice points onto the physical three-dimensional hyperplane is rationalized with the condition (1/1-1/1-1/1). This indicates that the Jones zone bounded by (10000) and (11000) planes in the icosahedral quasicrystal would play the same role as the (503), (532) and

(600) planes in the Frank–Kasper phase, thereby resulting in the same e/a dependence of the $\gamma_{\text{exp}}/\gamma_{\text{F}}$ in both phases.

Very recently, Wagner *et al* [12] reported the e/a dependence of the Hall coefficient, thermoelectric power and the electronic specific heat coefficient in Mg–Al–Cu and Mg–Ga–Zn quasicrystals. They drew a complicated curve passing through all data points of γ and claimed that the deviations occurring at about 2.2 and 2.4 e/a are caused by the Fermi surface–Brillouin zone interactions associated with (111101) and (210001) planes. Because of the experimental uncertainties, it seems to be a delicate matter to judge whether the singularities at 2.2 and 2.4 e/a , which they proposed, can be located in the present data shown in figure 3.

We found that the Frank–Kasper phase is thermodynamically stable regardless of the magnitude of $\gamma_{\text{exp}}/\gamma_{\text{F}}$. Indeed, the density of states at the Fermi level for the Frank–Kasper phase in the Mg–Al–Cu and Mg–Al–Ag alloy systems is found to be nearly free electron-like, whereas that for the Al–Li–Cu system is very small. The thermodynamically stable Al–Li–Cu quasicrystal is also characterized by the small ratio $\gamma_{\text{exp}}/\gamma_{\text{F}}$ [8]. The possession of a small value of γ_{exp} has been observed recently in the thermodynamically stable Al–Ru–Cu quasicrystal [13]. It has been argued that the stability of the quasicrystalline phase may be enhanced by adjusting the Fermi level to the position at the pseudogap in the density of states or the famous $2k_{\text{F}} = K_{\text{P}}$ criterion [9]. This statement seems to be valid, as far as the quasicrystalline phase is concerned. But, as noted above, it does not hold in the case of the Frank–Kasper crystal and/or a quasicrystal containing two electrons per atom in spite of the fulfilment of the $2k_{\text{F}} = K_{\text{P}}$ criterion. Some additional effects like the atomic size ratio must be taken into account in discussing the stability of these two phases in terms of e/a .

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