Magnetic properties of icosahedral quasicrystals and their cubic approximants in the Cd–Mg–RE (RE = Gd, Tb, Dy, Ho, Er, and Tm) systems

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Abstract
A systematic investigation has been performed to elucidate effects of rare earth type and structural complexity on magnetic properties of icosahedral quasicrystal (iQC) and their cubic approximants (APs) in the ternary Cd–Mg–RE (RE = Gd, Tb, Dy, Ho, Er, and Tm) systems. At low temperatures, iQCs and 2/1 APs exhibit spin-glass-like freezing for RE = Gd, Tb, Dy, and Ho, while for Er and Tm they do not show freezing behavior down to the base temperature \( \sim 2 \) K. The 1/1 APs exhibit either spin-glass-like freezing or antiferromagnetic (AFM) ordering depending on their constituent Mg content. The \( T_f \) values show increasing trend from iQC to 2/1 and 1/1 APs. In contrast, the absolute values of Weiss temperature for iQCs are larger than those in 2/1 and 1/1 APs, indicating that the total AFM interactions between the neighboring spins are larger in aperiodic, rather than periodic systems. Competing spin interactions originating from the long-range Ruderman–Kittel–Kasuya–Yoshida mechanism along with chemical disorder of Cd/Mg ions presumably account for the observed spin-glass-like behavior in Cd-Mg-RE iQCs and APs.

Keywords: quasicrystals, magnetism, spin glass, antiferromagnetism, magnesium alloys

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1. Introduction
Icosahedral quasicrystals (iQCs), as aperiodically-ordered intermetallic compounds, generate sharp Bragg reflections with 5-fold rotational symmetry, indicating the presence of a long-range positional order without periodicity in their atomic configuration [1, 2]. Based on their atomic structure, iQCs can be classified into three sub-types, namely the Mackay- [3], Bergman- [4] and Tsai-types [5]. The Tsai-type iQCs, in particular, including those found in the binary Cd–RE [6], ternary Cd-Mg-RE [7, 8] (RE = Y, Gd–Yb, where RE stands for ‘rare earth’), and Ag–In–Yb [9], and Au–Al–RE (RE = Yb, Tm) [10, 11] systems, are the most abundant in all the iQCs reported to date. Figure 1(a) illustrates shell structure of the basic cluster unit of Tsai-type iQCs [12, 13]. The magnetic properties of the Tsai-type iQCs in the Cd-RE and Cd-Mg-RE systems with trivalent REs (e.g. Y, Gd–Tm) have been investigated...
in a number of studies [14–19]. The results are summarized as follows: the temperature dependence of the magnetization follow the Curie–Weiss law at high temperatures. The effective magnetic moments are consistent with free RE$^{3+}$ ions. At low temperatures, these iQCs exhibit spin-glass-like freezing behavior. Meanwhile, short-range-magnetic correlations in the spin-glass-like state has been observed in the Cd–Mg–RE iQCs at low temperatures using neutron scattering [14]. The magnetic properties of the iQCs in both binary Cd–RE and ternary Cd–Mg–RE systems) are summarized in table 1.

In a close proximity of iQCs yet with slightly different compositions, the same rhombic tricontahedron (RTH) clusters can be arranged with translational symmetry generating their crystalline counterpart, so-called approximants (APs) [13]. 2/1 APs (space group, Pa$\bar{3}$) are structurally closer to iQCs (Pm$\bar{3}$5) than 1/1 APs (Im$\bar{3}$) [20, 21]. The configurations of RE atoms within the unit cells of the 1/1 and 2/1 APs are illustrated schematically in figures 1(b) and (c), respectively. Note that in the former, there exist 24 RE sites that are symmetrically equivalent. They form the icosahedral shells of the RTH clusters. In the latter, on the other hand, the 104 RE sites are divided into five Wyckoff orbits, represented by spheres of different colors in figure 1(c), all of which except RE4 belong to the icosahedral shells of the RTH clusters (see figure 1(a)). The four dimers of RE4 sites are arranged on the long body diagonals of the four acute rhombohedron units which fill in the gaps between the RTH clusters [12].

As represented in figure 2, the shortest RE–RE distances in both 1/1 and 2/1 APs (within a range of 3.4 to 6.2 Å) can be classified into the following seven categories: (I) icosahedral edge, (II) side edge of trigonal antiprisms, each of which has base triangles belonging to an adjacent pair of icosahedra aligned along a 3-fold axis, (III) side edge of rectangles, each of which connects parallel edges from an adjacent pair of icosahedra aligned along a 2-fold axis. For the 2/1 APs, additional categories are required: (IV-1, IV-2, and IV-3) three distinct distances between RE4 sites to icosahedral sites, and (V) short distance between two RE4 sites comprising a dimer associated with acute rhombohedron units. The 2- and 3-fold linkages between the cluster centers are represented by thick light blue and yellow bonds, respectively, in figures 1(b) and (c).

Magnetic properties of the Tsai-type 1/1 APs have been investigated in several systems. While ternary 1/1 APs tend to show spin-glass-like freezing, the binary Cd$_6$RE [15, 22–24] and ternary Au–SM–RE (RE = Gd and SM = Si, Ge) compounds [25–27] are of particular interest since they exhibit long-range antiferromagnetic (AFM) and ferromagnetic (FM) orderings, respectively. Moreover, the binary Cd$_6$RE compounds are reported to exhibit multiple anomalies in the temperature dependence of their magnetic susceptibilities (see table 1), indicating the existence of several distinct AFM phases [22, 23].

While no previous study has been reported on the magnetic properties of the APs in the ternary Cd–Mg–RE systems, it has recently been revealed that iQCs and their successive cubic 2/1 and 1/1 APs can be obtained in the ternary Cd–Mg–RE (RE = Gd, Tb, Dy, Ho, Er, and Tm) alloy systems.
Table 1. Magnetic properties of the binary Cd–RE and ternary Cd–Mg–RE (RE: rare earth) icosahedral quasicrystals (iQCs) and approximants (APs). $\Theta_w$ is the Weiss temperature, $T_f$ is the spin freezing temperature, $\mu_{\text{eff}}$ is the experimental effective moment and $\mu_{\text{calc}}$ is the calculated free-ion value.

| iQC/AP System       | $\mu_{\text{eff}}$ ($\mu_B/\text{REion}$) | $\mu_{\text{calc}}$ ($\mu_B/\text{REion}$) | $\Theta_w$ (K) | $T_f$ (K) | $T_{N1}$ (K) | $T_{N2}$ (K) | $T_{N3}$ (K) | $T_{N4}$ (K) | Reference |
|---------------------|------------------------------------------|------------------------------------------|----------------|-----------|-------------|-------------|-------------|-------------|-----------|
| iQC Cd$_{62}$Mg$_{35}$Gd$_{10}$ | 7.24                                     |                                          | -37.8          | 4.3       |             |             |             |             | [34]      |
| iQC Cd$_{62}$Gd    |                                          |                                          | -41            | 4.6       |             |             |             |             | [18]      |
| 1/1 AP Cd$_{62}$Gd | 7.94                                     | 7.94                                    | -32            | 18.9      | 13.2        | 7.3         | 2.5         |             | [23]      |
| iQC Cd$_{62}$Mg$_{35}$Tb$_{10}$ | 9.74                                     |                                          | -24.5          | 5.9       |             |             |             |             | [16, 34] |
| iQC Cd$_{62}$Tb    |                                          |                                          | -21            | 5.3       |             |             |             |             | [18]      |
| 1/1 AP Cd$_{62}$Tb | 9.8                                      | 9.72                                    | -17            | 24        | 19          | 2.4         |             |             | [22, 23] |
| iQC Cd$_{62}$Mg$_{35}$Dy$_{10}$ | 10.59                                    |                                          | -18.4          | 3.2       |             |             |             |             | [34]      |
| iQC Cd$_{62}$Dy    |                                          |                                          | -11            | 3         |             |             |             |             | [18]      |
| 1/1 AP Cd$_{62}$Dy | 10.9                                     | 10.63                                   | -5.1           | 17.8      |             |             |             |             | [23]      |
| iQC Cd$_{62}$Mg$_{35}$Ho$_{10}$ | 10.42                                    |                                          | -7             | 12.5      |             |             |             |             | [34]      |
| iQC Cd$_{62}$Ho    |                                          |                                          | -6             | 1.76      |             |             |             |             | [18]      |
| 1/1 AP Cd$_{62}$Ho | 10.5                                     | 10.60                                   | -1             | 8.4       | 6.8         | 3.4         |             |             | [23]      |
| iQC Cd$_{62}$Mg$_{35}$Er$_{10}$ | 9.71                                     |                                          | -6             | 4.4       |             |             |             |             | [34]      |
| iQC Cd$_{62}$Er    |                                          |                                          | -4             | 1.11      |             |             |             |             | [18]      |
| 1/1 AP Cd$_{62}$Er | 9.1                                      | 9.59                                    | -0.9           | 2.8       |             |             |             |             | [23]      |
| iQC Cd$_{62}$Mg$_{35}$Tm$_{15}$ | 7.08                                     |                                          | -2             |           |             |             |             |             | [34]      |
| iQC Cd$_{62}$Tm    |                                          |                                          | -2             | 0.63      |             |             |             |             | [18]      |
| 1/1 AP Cd$_{62}$Tm | 7.4                                      | 7.57                                    | -3.1           | 2.2       |             |             |             |             | [23]      |

Figure 2. Seven categories of shortest RE–RE distances in the 1/1 and 2/1 APs (within a range of 3.4 to 6.2 Å). (a) An edge of an icosahedron (I) and a side edge of a trigonal antiprism connecting triangular faces of adjacent icosahedra aligned along a 3-fold axis (II). (b) A side edge of a rectangle connecting parallel edges from adjacent icosahedra aligned along a 2-fold axis (III). (c) Three kinds of distances between an RE$_4$ site to icosahedral sites (IV-1, IV-2, and IV-3) as well as a short distance within an RE$_4$–RE$_4$ dimer (V). (a) and (b) are common arrangements to both the 1/1 and 2/1 APs, whereas (c) is for the 2/1 AP only. The typical values of distances for the Cd–Mg–Er 2/1 AP are as follows: (I): 5.73 Å, (II): 5.75 Å, (III): 6.12 Å, (IV-1): 6.04 Å, (IV-2): 5.64 Å, (IV-3): 5.59 Å, and (V): 3.47 Å.

This allows us to perform a systematic investigation of the magnetic properties of iQCs, 2/1 and 1/1 APs, and is likely to provide important insights into the nature of magnetic freezings in aperiodic systems. The present research, therefore, intends to perform magnetic susceptibility measurements on iQCs, 2/1 and 1/1 APs in the Cd–Mg–RE (RE = Gd, Tb, Dy, Ho, Er, and Tm) systems to show if there are any systematic trends, which could possibly serve as a useful guideline for tuning or tailoring the magnetic properties.

2. Experiment

As-cast Cd–Mg–RE (RE = Gd, Tb, Dy, Ho, Er, and Tm) alloys were prepared by encapsulating three grams of starting elements into stainless-steel tubes employing arc-welding under Ar atmosphere. The tubes were further placed inside quartz tubes under depressurized Ar gas (∼550 Torr). Based on the developed pseudo-binary phase diagram [28, 29], the APs are stable at ∼773 K, while the iQCs are stabilized at lower temperatures. Except the 2/1 APs that have very strict compositions (i.e., Cd$_{62.65}$Mg$_{22.25}$RE$_{13}$), both the 1/1 APs and iQCs occur inside relatively large and elongated single-phase domains with varying Cd/Mg ratios in the ternary phase diagrams. Such a high solubility of Mg in the Cd-based systems is usually discussed by almost similar atomic size and valence number of Mg and Cd whereby the replacement of Cd by Mg would thus not cause much strain or change in electron concentration. However, for unknown reasons, the single domains of the 1/1 APs, i.e., (Cd, Mg)$_6$RE, behave differently depending on the RE element. The largest domain is observed for RE = Tb, where it spans up to Cd$_{65}$Mg$_{20}$RE$_{15}$ in the ternary phase diagram. For RE = Dy, Ho and Er, on the other hand, the single 1/1 AP domains shrink to ≈10 at% Mg. Given that the 2/1 AP forms inside a very strict compositional area close to Cd$_{63.5}$Mg$_{22.5}$RE$_{14}$, we tried to keep the Mg content of the iQCs and 1/1 APs as close as possible to ≈20–25 at%. Consequently, alloys with nominal compositions...
of Cd_{65}Mg_{22.5}Gd_{13}, Cd_{62}Mg_{25}Tb_{13} and Cd_{65+x}Mg_{20−x}RE_{15} (x = 0 for RE = Tb, and x = 10 for RE = Dy, Ho, Er) were carefully selected to synthesize single-phase polycrystalline iQCs, 2/1 and 1/1 APs, respectively. Despite several attempts, no 2/1 AP but only 1/1 AP is detected in an alloy with nominal composition of Cd_{65}Mg_{22}Gd_{13}. Investigating the effects of Mg addition on magnetic behaviors of the 1/1 APs falls outside the scope of the current paper and thus is left for future work. The heat treatment protocols for synthesizing iQC and APs are as follows: after an initial melting of the prepared alloys at 973 K, iQC and APs were isothermally annealed at 673 K for over 140 h and 773 K for over 100 h, respectively. Microstructures and local compositions of the prepared samples were analyzed by scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) spectrometer. The specimens for TEM observation were prepared using ‘crush-and-float’ method during which the samples were crushed in ethanol for TEM observation were prepared using ‘crush-and-float’ method during which the samples were crushed in ethanol and lightly floated pieces were then transferred to a Cu grid. For electron backscatter diffraction (EBSD) analysis, the surface of the samples was polished by ion bombardment machine with accelerated voltage, gun current, milling time and ion angle of 2 kV, 2 mA, 3 h, and 12°, respectively. Powder x-ray diffractometry (XRD; Rigaku Ultima IV) with Cu-Kα was used for the phase identification of the prepared alloys. The temperature dependence of the dc magnetic susceptibility was measured in a temperature range of 2–300 K under 100 Oe using superconducting quantum interfering device (SQUID) magnetometer (Quantum Design, MPMS-XL). The data collection was conducted for both zero-field cooled (ZFC) and field cooled (FC) conditions. The ac magnetic susceptibility measurements were carried out with frequencies varying from 1 to 100 Hz in a temperature range of 2–20 K under zero external magnetic field.

### 3. Results and discussion

The nominal and analyzed compositions of the investigated samples are listed in table 2. The table evidences a good agreement between the two sets of values. Detailed elemental analyses as well as the obtained EDX spectra from all the samples are provided in the supplementary information (stacks.iop.org/JPCM/32/415801/mmedia). The obtained data show no sign of Fe, O, or C as a possible contamination from the synthesis procedure. Typical backscattering SEM images from microstructures of the Cd_{65}Mg_{25}Tb_{13}, Cd_{62}Mg_{25}Tb_{13} and Cd_{68}Mg_{25}Tb_{13}, which can be assigned as single-phase iQC, 2/1 and 1/1 APs, are presented in figures 3(a)–(c). The EDX analysis of the specified regions are shown on top right corner of the images. The atomic concentration of the magnetic Tb shows gradual increase from 12.56 at% in iQC to 14.26 at% in 1/1 AP. The corresponding EBSD Kikuchi patterns are displayed in figures 3(d)–(f). As shown, the iQC and 2/1 AP exhibit almost undistinguishable patterns with obvious pentagon-shaped Kikuchi bands, at the center of which the bands intersect at a unique point (marked as 5-fold [211 111] and pseudo-5-fold [805] in iQC and 2/1 AP, respectively). This indicates high resemblance in atomic structures of the iQC and 2/1 AP. However, the Kikuchi pattern obtained from the 1/1 AP reveals split Kikuchi bands forming a distorted pentagonal band with pseudo-5-fold [503] pole at the center suggesting a significant deviation of the 1/1 AP structure from the iQC one. Figures 3(g)–(i) provide selected area electron diffraction (SAED) patterns of the iQC and APs taken with incidences along their 3-fold axes. As seen, while the iQC represents sharp diffraction spots inflating in τ order, the pattern obtained from the 2/1 AP in figure 3(h) exhibits zig-zag array of diffraction peaks (indicated by arrows) originating from a linear phonon phase in the atomic structure [30]. The SAED pattern of the 1/1 AP in figure 3(i) represents a larger displacement of diffraction spots from ideal positions indicating a larger magnitude of linear phonon strain in the structure compared to the 2/1 AP. The results provided in figure 3 evidence a systematic and successive deviation of the atomic structure in, respectively, 2/1 and 1/1 APs from an ideal iQC symmetry. This is of special interest in the present study since it offers a unique opportunity to obtain a possible trend in their magnetic behavior by performing magnetic susceptibility measurements.

Table 2. Nominal and analyzed compositions of the investigated alloys

| iQC/AP | Nominal composition | Analyzed composition |
|--------|---------------------|----------------------|
| iQC    | Cd_{65}Mg_{22}Gd_{13} | Cd_{65.42}Mg_{22.93}Gd_{12.65} |
| 1/1 AP | Cd_{65}Mg_{22}Gd_{13} | Cd_{65.42}Mg_{22.93}Gd_{12.65} |
| iQC    | Cd_{62}Mg_{25}Tb_{13} | Cd_{62.53}Mg_{24.95}Tb_{13.29} |
| 2/1 AP | Cd_{62}Mg_{25}Tb_{13} | Cd_{62.53}Mg_{24.95}Tb_{13.29} |

where p and q indicates AP indices, e.g., p = 1, q = 2 for 2/1 AP, and τ is the golden mean [20]. Clearly, a_q increases from 5.588 Å for the CdMgTm 2/1 AP to 5.652 Å for i-CdMgGd. Provided that the RTH structure is identical, such increment of a_q in i-QCs can be viewed as the effect of RE atomic size on the expansion of the RTH cluster.
Figure 3. (a)–(c) Backscattered scanning electron microscopy (SEM) images, (d)–(f) electron backscatter diffraction (EBSD) Kikuchi patterns and (g)–(i) selected area electron diffraction (SAED) patterns taken with incidences along 3-fold axes of (a, d, g) iQC, (b, e, h) 2/1 AP and (c, f, i) 1/1 AP in the Cd–Mg–Tb system. The energy dispersive x-ray (EDX) analysis of specific regions are shown on top right corner of the figures (a)–(c).

Figure 4. Variation of the quasilattice parameter ($a_q$), defined as the edge length of the RTH clusters in Cd–Mg–RE iQCs (Cd$_{65}$Mg$_{22.5}$RE$_{12.5}$), 2/1APs (Cd$_{62}$Mg$_{25}$RE$_{13}$) and 1/1 APs (Cd$_{65}$Mg$_{20}$Tb$_{15}$ and Cd$_{65}$Mg$_{22}$Gd$_{13}$) consisting 20–25 at% Mg.

Figure 5 presents the temperature dependence of the dc magnetic susceptibility ($\chi$) and inverse magnetic susceptibility ($1/\chi$) for the iQC and APs measured under 100 Oe in the temperature range of 2–300 K. The magnified low-temperature susceptibilities from 2 to 30 K are also shown in the inset. Open and filled circles in figure 5 represent FC and ZFC curves, respectively. At high temperatures ($100 \text{ K} < T < 300 \text{ K}$), the temperature dependence of inverse magnetic susceptibility in all samples falls on a line following the Curie–Weiss law:

$$\chi(T) = \chi_0 + \frac{N_A \mu_{\text{eff}}^2 \mu_B^2}{3k_B(T - \theta_w)}$$

(2)

where $N_A$, $k_B$, $\mu_B$, $\mu_{\text{eff}}$, $\theta_w$ and $\chi_0$ are Avogadro’s number, the Boltzmann factor, Bohr magneton, effective magnetic moment, Weiss temperature and the temperature-independent magnetic susceptibility, respectively. $\theta_w$ values representing a sum of all exchange interactions are obtained by extrapolating the least-squares fitting of the susceptibility data within 100–300 K to the temperature axis. It turns out that the values of $\chi_0$ for all investigated samples fall within a range of $-0.01$ to $-0.005$, which are comparable to the experimental uncertainties, so that $\chi_0$ is henceforth assumed to be 0. The freezing temperature $T_f$ was obtained from the cusp on the ZFC curve. The transition temperature $T_N$ for AFM ordering was also obtained from the cusp on the ZFC and FC curves. Table 3 summarizes the estimated $\mu_{\text{eff}}$, $\theta_w$, and $T_f$ or $T_N$. The

Table 3 summarizes the estimated $\mu_{\text{eff}}$, $\theta_w$, and $T_f$ or $T_N$. The
uncertainty in estimation of $\theta_w$ corresponds to standard deviation arising from least-squares fitting of the susceptibility data over different temperature ranges. As seen, the effective moments $\mu_{\text{eff}}$ are close to the calculated values for free RE$^{3+}$ ions, $\mu_{\text{Re}^{3+}} = g\sqrt{J(J+1)}\mu_B$ (where $g$ and $J$ stand for the Landé $g$-factor and total magnetic angular moment, respectively), indicating that RE atoms are trivalent. Moreover, all samples exhibit negative $\theta_w$ values, indicating that RE–RE exchange interactions are dominantly antiferromagnetic.

At low temperatures, as shown in the insets of figure 5, the magnetic susceptibility of the iQC and 2/1 APs for the RE atoms except Tm and Er exhibits bifurcation between the ZFC and FC curves below $T_f$. Such bifurcation is associated with the spin-glass-like freezing. For further confirmation of the spin-freezing phenomenon, the temperature dependence of the ac magnetic susceptibility of the 2/1 AP in the Cd–Mg–Ho system was measured under selected frequencies between 1 to 100 Hz. The result is shown in figure 6(a). The position of the cusp ($T_f$) is shifted about 0.6 K to the higher temperatures, and the magnitude is reduced by 9.43%, as the frequency is increased from 1 to 100 Hz. The imaginary part $\chi''$ in figure 6(b) illustrates a sharp rise near $T_f$. Such a frequency dependent variation of the $\chi''$ offers a reliable criterion for distinguishing a spin-glass-like material from other magnetic systems [31, 32]. Note that this is the first observation of the spin-glass-like feature in the cubic 2/1 and 1/1 APs in the ternary Cd–Mg–RE systems. In the case of iQCs (RE = Ho and Er), 2/1 and 1/1 APs (RE = Er and Tm) no cusp has been observed down to 2 K.

For some of the samples, such as the iQC and 1/1 AP in the Cd-Mg-Tb system, the cusps in both the ZFC and FC susceptibility curves shown in figure 5 are smoothen out significantly. Such behavior accords with earlier observations in Tb-contained binary i-CdREs [18] and ternary i-CdMgREs [16] and may possibly originate from a gradual blocking of the spin rotations causing the magnetic system to slowly fall into the frozen state. Sebastian et al. [16], however, associated such behavior with a possible presence of magnetic impurities such as oxides. Moreover, magnetic susceptibilities in figures 5(c) and (e) evidence separation of the FC and ZFC curves at higher temperatures than the $T_f$ for iQC and APs in Cd–Mg–RE (RE = Tb and Dy) systems. This behavior is also consistent with earlier reports in binary i-Cd–Dy/Tb [6] and ternary i-Cd–Mg–Tb [16] systems and is attributed to the intrinsic tendency of these compounds to have a distribution in freezing temperature [14]. In figures 5(e) and (g), the low temperature magnetic susceptibility of the 1/1 APs in Cd–Mg–RE (RE = Dy and Ho) systems is shown. It does not exhibit spin-glass-like bifurcation of FC and ZFC but a conventional AFM ordering; one sharp anomaly at $T_N = 7$ K in Cd$_{75}$Mg$_{10}$Ho$_{15}$ and two anomalies at $T_N = 5$ and 11 K in Cd$_{75}$Mg$_{10}$Dy$_{15}$, are clearly seen in figures 5(e) and 5(g). The magnetic ordering in these compounds may originate from their lower Mg content (i.e. 10 at%), compared to the rest of the alloys that contain 20–25 at% Mg (see table 3). One may expect substantially less chemical disorder for the Cd/Mg mixed sites, and this less disorder may suppress the spin-glass freezing, resulting in the AFM ordering, as commonly

Figure 5. Temperature dependence of the (a, c, e, g, j, l) magnetic susceptibilities and (b, d, h, k, m) inverse magnetic susceptibilities of the iQC, 2/1 and 1/1 APs in the Cd–Mg–RE (RE = Gd, Tb, Dy, Ho, Er and Tm) systems measured under $H = 100$ Oe showing both field cooled (FC) and zero field cooled (ZFC) behaviors. Open and close circles represent FC and ZFC curves, respectively.
On the other hand, the linear scaling for $T_f$ is less obvious; serious deviation can be found for $RE = Gd$. This is most likely due to the difference in the single ion anisotropy; because of the vanishing orbital component, $Gd^{3+}$ is exceptionally isotropic among other $RE$ ions in crystalline electric field, giving rise to the lower transition temperature. In addition to the de Gennes scaling, the $T_f$ is largest for 1/1 AP, while the smallest $T_f$ is found for iQC. In striking contrast, the $\theta_w/\theta_0$ values for iQCs are larger than those in 2/1 and 1/1 APs, respectively, suggesting that the total AFM interaction is increasing from 1/1 AP to 2/1 AP and further to the iQC. This indicates that the empirical frustration parameter $\theta_w/\theta_0$ is largest for 1/1 AP, while the smallest $\theta_w/\theta_0$ is found for iQC. In other magnetic systems, such as 10 in binary Cd–Gd [6], 4.5 in ternary Zn–Mg–Tb [35, 36], 2.4–17 in ternary Ag–In–RE [37], and 2.3–3.6 in ternary Au–Al–Tm [38] systems. Larger $\theta_w/\theta_0$ values for iQCs than APs (see table 3). The same conclusion can also be drawn by careful inspection of the magnetic parameters for the binary Cd–RE iQCs and 1/1 APs, as summarized in table 1.

Large $\theta_w/\theta_0$ values have also been reported in iQCs and APs in other alloys systems such as 10 in binary Cd–Gd [6], 4.5 in ternary Zn–Mg–Tb [35, 36], 2.4–17 in ternary Ag–In–RE [37], and 2.3–3.6 in ternary Au–Al–Tm [38] systems. Larger $\theta_w/\theta_0$ values for iQCs than APs may be interpreted as an evidence for higher competition of the magnetic interactions in aperiodic, rather than periodic systems.

To gain some insight into the difference in the competitions of interactions between iQC and APs, we show the multiplicity of $RE^{3+}$–$RE^{3+}$ distances and the distance dependence of Ruderman–Kittel–Kasuya–Yosida (RKKY)-type interactions. Larger $\theta_w/\theta_0$ values for iQCs than APs may be interpreted as an evidence for higher competition of the magnetic interactions in aperiodic, rather than periodic systems.

Table 3. Weiss temperature ($\theta_w$), the freezing temperature ($T_f$), and effective magnetic moment ($\mu_{eff}$) of the iQC, 2/1 and 1/1 APs

| iQC/AP | Composition | $\mu_{eff}$ ($\mu_B$/RE atom) | $\mu_{calc}$ ($\mu_B$/RE atom) | $\theta_w$ (K) | $T_f$ (K) | $T_N$ (K) | $|$|\theta_w/T_f||
|---|---|---|---|---|---|---|---|
| iQC | Cd$_{65}$Mg$_{22.5}$Gd$_{12.5}$ | 7.8 ± 0.2 | 7.94 | -31.0 ± 1.5 | 5.0 ± 0.5 | — | 6.2 ± 1.5 |
| 1/1 AP | Cd$_{65}$Mg$_{22.5}$Gd$_{12.5}$ | 7.6 ± 0.2 | -26.5 ± 1.5 | 12.5 ± 0.5 | — | 2.0 ± 1.5 |
| iQC | Cd$_{65}$Mg$_{22.5}$Tb$_{12.5}$ | 9.8 ± 0.2 | 9.72 | -25.5 ± 1.5 | 6.0 ± 0.5 | — | 5.1 ± 1.5 |
| 2/1 AP | Cd$_{65}$Mg$_{22.5}$Tb$_{12.5}$ | 9.8 ± 0.2 | -23.0 ± 1.5 | 11.0 ± 0.5 | — | 2.0 ± 1.5 |
| 1/1 AP | Cd$_{65}$Mg$_{22.5}$Tb$_{12.5}$ | 9.7 ± 0.2 | -17.5 ± 1.5 | 13.0 ± 0.5 | — | 1.3 ± 1.5 |
| iQC | Cd$_{65}$Mg$_{22.5}$Dy$_{12.5}$ | 10.8 ± 0.2 | 10.63 | -17.0 ± 2.0 | 3.0 ± 0.5 | — | 5.5 ± 1.5 |
| 2/1 AP | Cd$_{65}$Mg$_{22.5}$Dy$_{12.5}$ | 10.6 ± 0.2 | -13.5 ± 1.5 | 4.0 ± 0.5 | — | 2.7 ± 1.5 |
| 1/1 AP | Cd$_{65}$Mg$_{22.5}$Dy$_{12.5}$ | 10.0 ± 0.2 | -8.0 ± 2.0 | — | 11.0 ± 0.5 | 0.8 ± 1.5 |
| iQC | Cd$_{65}$Mg$_{22.5}$Ho$_{12.5}$ | 10.7 ± 0.2 | 10.60 | -7.0 ± 2.0 | — | — |
| 2/1 AP | Cd$_{65}$Mg$_{22.5}$Ho$_{12.5}$ | 10.5 ± 0.2 | -5.5 ± 1.5 | 4.0 ± 0.5 | — | 1.7 ± 1.5 |
| 1/1 AP | Cd$_{65}$Mg$_{22.5}$Ho$_{12.5}$ | 10.2 ± 0.2 | -4.0 ± 1.5 | — | 7.0 ± 0.5 | 0.8 ± 1.5 |
| iQC | Cd$_{65}$Mg$_{22.5}$Er$_{12.5}$ | 9.6 ± 0.2 | 9.59 | -3.5 ± 1.5 | — | — |
| 2/1 AP | Cd$_{65}$Mg$_{22.5}$Er$_{12.5}$ | 9.5 ± 0.2 | -4.0 ± 1.5 | — | — |
| 1/1 AP | Cd$_{65}$Mg$_{22.5}$Er$_{12.5}$ | 9.3 ± 0.2 | -1.5 ± 1.5 | — | 2.5 ± 0.5 | 0.5 ± 1.5 |
| 2/1 AP | Cd$_{65}$Mg$_{22.5}$Tm$_{13}$ | 7.2 ± 0.2 | 7.57 | -0.5 ± 1.5 | — | — |

Figure 6. (a) The real and (b) imaginary parts of the ac susceptibility of the Cd–Mg–Ho 2/1 AP measured under $f_e = 1–100$ Hz.
interaction in figure 8. For indirect RKKY-type interactions, the interaction strength oscillates with distance between the spins \(r\) and fades away in sufficiently long-ranged distances as \((1/r)^3\) [23, 31, 39]. By assuming a free-electron model, the coupling constant \(J(r)\) between spins is expressed by the following relation [39]:

\[
J(r) = -\pi \frac{N}{V} \frac{J_0}{\varepsilon_F} f \left(2k_Fr_j\right),
\]

where \(f(x)\) is given as:

\[
f(x) = (-x \cos x + \sin x) / x^4.
\]

In equation 3, \(N/V, J_0, \varepsilon_F, r_j\) and \(k_F\) denote the number of electrons per unit cell, the RKKY coupling strength, the Fermi energy, the distance between two spins and the Fermi wave vector. Under the approximation of spherical symmetry, the Fermi wave vector is determined as:

\[
k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}
\]

which only depends on the electron concentration.

The oscillatory behavior of the RKKY interaction leads to the occurrence of competing FM and AFM interactions alternatively [31]. Based on the preliminary structure analysis [40], the 1/1 and 2/1 AP unit cells contain 176 and 702 atoms, respectively. By assuming Cd and Mg to be divalent and RE elements to be trivalent (based on the obtained effective moments in table 3), the number of free electrons within a unit cell is estimated to be 376 and 1482 in 1/1 and 2/1 APs, respectively. Considering the lattice parameter of the 1/1 AP (resp. 2/1 AP) to be 1.54 (resp. 2.49 nm), the Fermi wave vector \(k_F\) is calculated to be \(1.45 \times 10^{10}\) m\(^{-1}\) (resp. \(1.44 \times 10^{10}\) m\(^{-1}\)). Note that the afore-mentioned structure parameters of the 1/1 and 2/1 AP belong to, respectively, Cd–Mg–Y and Cd–Mg–Er systems, as typical examples. Figure 8 plots variation of \(f(2k_Fr_j)\) and distribution of RE\(^{3+}\) spins as a function of interspin distance \(r_j\) for 1/1 and 2/1 APs up to 10 Å. Note that each set of the symmetrically equivalent REs in the 2/1 AP, i.e. RE\(_{1–3}\)–RE\(_{5}\), as illustrated in figure 2, has distinct local environment and thus exhibits different distribution of RE–RE distances in figures 8(b)–(f). A bin width of \(\delta = 0.07\) Å is applied to the histograms of nearest-neighbor distances. While multiple RE\(^{3+}\)–RE\(^{3+}\) distances exist in the 2/1 AP (figures 8(b)–(f)), only a few ones occur in the 1/1 AP (figure 8(a)). This larger variation of interspin distances in 2/1 AP may result in much pronounced competition for 2/1 AP. This explains the measured larger \(|\theta_u/T_1|\) values for the 2/1 AP in table 3 compared to those obtained for 1/1 AP. Taking into account high structural resemblance between the iQC and 2/1 AP [12], it may be reasonable to assume that the RE\(^{3+}\) spin distribution and RKKY oscillation in the iQC would be similar to that of the 2/1 AP, presumably resulting in similar or even more pronounced competition of magnetic interactions in iQC. Note that similar approach using simplest free-electron model was already applied to explain composition-driven spin glass to ferromagnetic transition in the quasicrystal approximant in the Au–Al–Gd system [39]. It should be mentioned that although figure 8 captures an unevenness in the RE–RE pair distributions and thus evidences a more pronounced competition among FM and AFM exchanges in the 2/1 AP than 1/1 AP using the free-electron model, it is still deficient in depicting realistic RKKY oscillation regarding the sign of the \(J(r)\). Resolving this inconsistency requires more quantitative analysis, whereby it is necessary to go beyond the simplest free-electron model.

We note that to discuss the origin of the spin-glass behavior in the present samples, the chemical disorder of the Cd/Mg should be taken into account. This can be inferred from the observation that the long-range antiferromagnetic order in the 1/1 APs with less Mg composition is replaced by the spin-glass-like freezing by increasing Mg composition. One may
also consider the orientational disorder of the central tetrahedron of the RTH clusters as another source of disorder contributing to the observed spin-glass-like behavior of the present samples. This kind of disorder was considered to be magnetically equivalent to the chemical disorder in iQC and APs in ternary Au–Al–RE systems [38, 41], which are isostructural with those in Cd–RE system. Quite recently, the importance of the chemical disorder was also indicated directly by measuring crystalline-electric-field splitting in Au–Si–Tb 1/1 AP [42]. Therefore, it seems reasonable to assume that the combination of chemical disorder and competition between FM and AFM couplings due to oscillating RKKY interaction is responsible for the spin-glass-like feature in the present samples.

4. Conclusion

The present research set out to compare the magnetic properties of the iQC, 2/1 and 1/1 APs in the ternary Cd–Mg–RE (RE = Gd–Tm) systems. The conclusions drawn are as follows: At higher temperatures (100 K < T < 300 K), all the iQCs and APs follow the Curie–Weiss law. The estimated $\mu_{\text{eff}}$ are close to the calculated values for free RE$^{3+}$. The $\theta_w$
values are negative indicating that RE–RE exchange interactions are dominantly AFM. On the other hand, at lower temperatures, iQCs and 2/1 APs exhibit spin-glass-like anomalies for the RE atoms except Tm and Er. The 1/1 APs exhibit either spin-glass-like freezing or AFM ordering depending on Mg content. The Tg values show increasing trend from iQC to 2/1 and 1/1 APs. In contrast, |\theta_g| values for iQCs are larger than those for 2/1 and 1/1 APs, indicating that the total AFM interactions between the adjacent spins are larger in aperiodic systems than periodic ones. The combination of chemical disorder and competition between FM and AFM couplings due to the oscillating RKKY interaction, is presumably responsible for the spin-glass-like feature that is observed in most of the present compounds.

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