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Structural-transition-driven antiferromagnetic to spin-glass transition in Cd–Mg–Tb 1/1 approximants

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Abstract

The magnetic susceptibility of the 1/1 approximants to icosahedral quasicrystals in a series of $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 10, 15, 20$) alloys was investigated in detail. The occurrence of antiferromagnetic (AFM) to spin-glass (SG)-like transition was noticed by increasing Mg. Transmission electron microscopy analysis evidenced a correlation between the magnetic transition and suppression of the monoclinic superlattice ordering with respect to the orientation of the Cd_4 tetrahedron at $T > 100$ K. The possible origins of this phenomenon were discussed in detail. The occurrence of the AFM to SG-like magnetic transition is associated with the combination of chemical disorder due to a randomized substitution of Cd with Mg and the orientational disorder of the Cd_4 tetrahedra.

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

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Quasicrystals have been an object of research since their initial discovery in 1984 [1]. They are characterized as solid state materials possessing a particular kind of long-range order without periodicity in their atomic configuration [2]. Tsai-type icosahedral quasicrystals (iQCs), in particular, exhibiting an icosahedral point symmetry consist of rare earth (RE) elements along with Cd or a mix of two metallic species following the substitution rules [3–5]. Their atomic structure is composed of a kind of clusters with five successive shells [6–8]; as seen in figure 1(a). Generally, their temperature-dependent

magnetization at high temperatures (except $\text{RE} = \text{Yb}$, which is divalent in the iQCs) follows the Curie–Weiss law with effective magnetic moments being consistent with free RE^{3+} ions. At low temperatures, spin-glass (SG)-like freezing behavior has been reported for iQCs [9–12].

In the near proximity of iQCs in some alloy systems, in terms of chemical composition, there exist compounds that contain the same rhombic triacontahedron (RTH) clusters being arranged in a body-centred cubic (bcc) packing rather than in aperiodic manner [13, 14]. These compounds are known as 1/1 approximants (APs). The configuration of RE atoms within the unit cell of the Tsai-type 1/1 AP is illustrated schematically in figure 1(b). Amongst the known 1/1 APs, the binary Cd_6RE [11, 15–17], ternary Au–Al–RE

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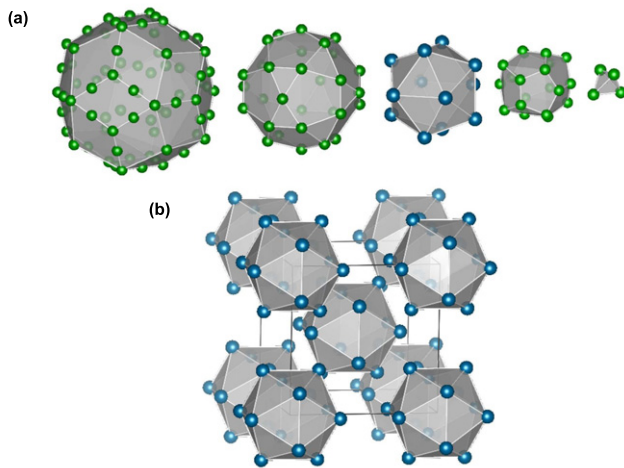


Figure 1. (a) Shell structure of the Tsai-type iQC. From left to right: Cd rhombic tricontahedron (RTH) (92 atoms), Cd icosidodecahedron (30 atoms), RE icosahedron (12 atoms), Cd dodecahedron (20 atoms), and inner Cd tetrahedron (4 atoms). (b) RE sites on the icosahedron shell of the RTH clusters in the atomic structures of the 1/1 AP in Cd_6Tb compound.

and Au–SM–RE systems (RE = rare earth, SM = Si, Ge or Sn) [18–20] have received considerable attention since they exhibit a long-range magnetic ordering at low temperatures. The binary Cd_6RE compounds, in particular, exhibit an anti-ferromagnetic (AFM) ordering evidenced by one or several anomalies in their magnetic susceptibilities [15, 16].

One of the unique features of the compounds in the Cd–RE systems is that they show high solubility of Mg atoms that locate on Cd sites due to their almost similar atomic size and valence. This leads to a rather elongated single-phase region for iQC or 1/1 AP in the ternary Cd–Mg–RE phase diagrams [21, 22]. For example, the single phase region of 1/1 AP in the Cd–Mg–Tb system spans up to $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$. This paper, therefore, aims to study the consequences of Mg addition on the magnetic properties of 1/1 APs in the Cd–Mg–Tb system especially focusing on the relevance of minor changes in the crystal structure. The AFM to SG-like transition is noticed to be triggered by increasing Mg content of the alloys. Such magnetic transition is associated with order–disorder-type phase transition with respect to the orientation of the central Cd_4 tetrahedron. The results indicate that Mg addition effectively suppresses the ordering of Cd_4 tetrahedra, which is a key element in the occurrence of AFM magnetic transition.

2. Experiment

Polycrystalline samples of $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 6, 7.5, 10, 12.5, 15, 17.5, 20$) 1/1 APs were prepared first by loading three grams in total of pure Cd (99.99%), Mg (99.9999%) and Tb (99.9999%) into stainless-steel tubes and sealed with Ar gas employing arc-welding. The tubes were further sealed in quartz tubes under an Ar gas atmosphere (~ 550 Torr). After an initial melting of the prepared alloys at 973 K, they were isothermally annealed at 773 K for 100 h. In order to evaluate the phase quality of the resulting alloys, powder

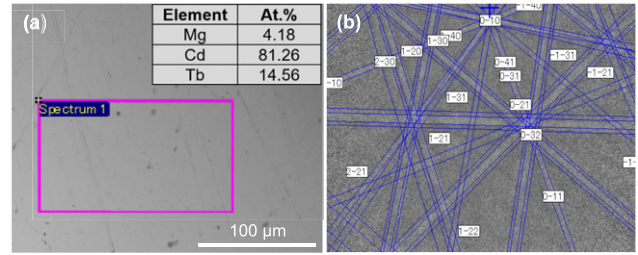


Figure 2. (a) Backscattered SEM image from a microstructure of the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ 1/1 AP. The EDX analysis of specific region is shown on the top right corner. (b) EBSD Kikuchi pattern of the same sample. The pattern exhibits split Kikuchi bands forming distorted pentagonal bands with pseudo-five-fold $[0\bar{3}2]$ pole in the center suggesting a significant deviation of the 1/1 AP structure from an ideal iQC one.

x-ray diffractometry (XRD) was performed using $\text{Cu-K}\alpha$. In addition, the scanning electron microscopy (SEM; Hitachi SU-6600) equipped with energy dispersive x-ray (EDX) spectrometer was utilized to investigate the microstructure and local compositions of the prepared alloys. All the samples turned out to be single phase polycrystalline 1/1 APs, as described later. 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. For transmission electron microscopy (TEM) analysis, the samples were crushed in ethanol and transferred to a Cu grid. An energy-filter TEM JEM-2010FEF was used at an accelerating voltage of 100 kV with a liquid-nitrogen cooling specimen holder.

The temperature dependence of the magnetic susceptibility was measured between 2–300 K under an external DC field of 100 Oe using superconducting quantum interfering device magnetometer (Quantum Design, MPMS-XL). Both zero-field cooled (ZFC) and field cooled (FC) data were collected. The AC magnetic responses of two representative samples were measured within $2 < T < 300$ K and frequencies varying from 1 to 100 Hz with $H_{AC} = 3$ Oe.

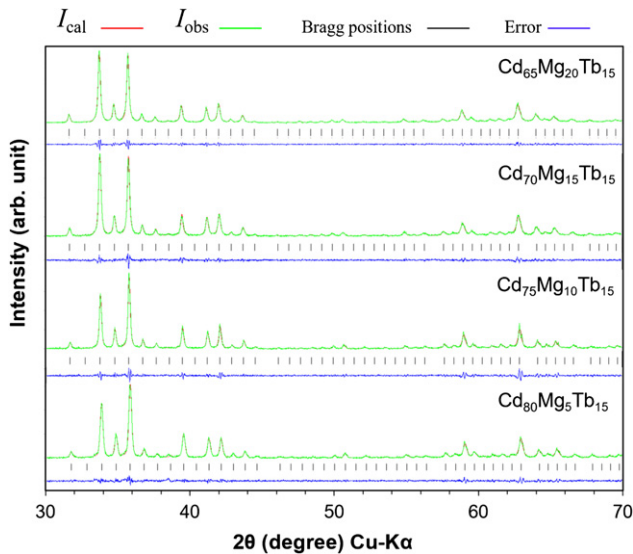
3. Results and discussion

Figure 2(a) shows a typical backscattered SEM image from a microstructure of the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ 1/1 AP annealed at 773 K for 100 h. The microstructure exhibits a homogeneous single phase. The EDX analysis of the specified region provided the composition values shown on the top right corner of the image, being consistent with the nominal values. Similar results were also obtained for the remaining samples, as listed in table 1. The obtained data show no sign of Fe, O or C as a possible contamination from the synthesis procedure. Figure 2(b) represents EBSD Kikuchi pattern taken from the sample. As provided elsewhere [21, 22], the deformed pentagonal shape of the Kikuchi bands surrounding the $[0\bar{3}2]$ pole, noticed by degenerate intersection of the Kikuchi bands as well as the occurrence of split diverging bands clearly differentiate the material from 2/1 AP and iQC, confirming that it is 1/1 AP.

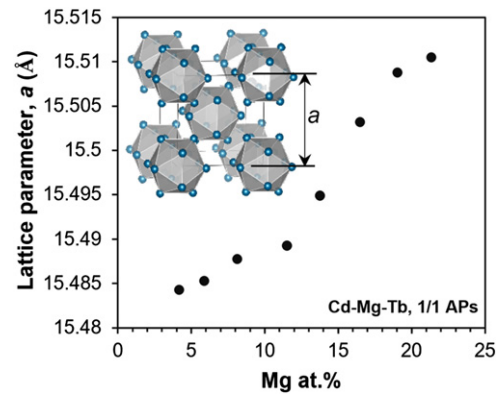
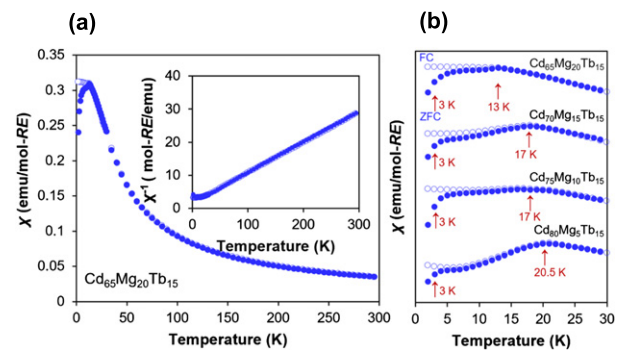
Figure 3 provides powder XRD patterns of selected $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 10, 15, 20$) alloys with their

Table 1. Nominal alloy compositions and analyzed compositions of the alloys examined in this study.

Nominal composition	Analyzed compositions
Cd ₈₀ Mg ₅ Tb ₁₅	Cd _{81.26} Mg _{4.18} Tb _{14.56}
Cd ₇₉ Mg ₆ Tb ₁₅	Cd _{79.17} Mg _{5.91} Tb _{14.92}
Cd _{77.5} Mg _{7.5} Tb ₁₅	Cd _{77.11} Mg _{8.14} Tb _{14.75}
Cd ₇₅ Mg ₁₀ Tb ₁₅	Cd _{74.18} Mg _{11.53} Tb _{14.29}
Cd _{72.5} Mg _{12.5} Tb ₁₅	Cd _{71.19} Mg _{13.86} Tb _{14.95}
Cd ₇₀ Mg ₁₅ Tb ₁₅	Cd _{68.7} Mg _{16.51} Tb _{14.79}
Cd _{67.5} Mg _{17.5} Tb ₁₅	Cd _{66.68} Mg _{19.06} Tb _{14.26}
Cd ₆₅ Mg ₂₀ Tb ₁₅	Cd _{64.09} Mg _{21.34} Tb _{14.57}

**Figure 3.** Calculated (red line) and measured (green line) powder x-ray diffraction (XRD) patterns of the Cd–Mg–Tb 1/1 APs containing 5, 10, 15 and 20 at% Mg after annealing at 773 K. Le Bail analysis is performed for the calculation. The blue line indicates the difference between the theoretical and experimental intensities, while black vertical bars show the Bragg peak positions.

corresponding Le Bail refinements [23] in the space group of $Im\bar{3}$ using Jana 2006 software suite [24]. Measured peak intensities (I_{obs}) and calculated peak intensities (I_{cal}) in the figure are represented by green and red solid lines, respectively. The difference between the theoretical and experimental intensities ($I_{cal} - I_{obs}$) is represented by a blue line, while the expected Bragg peak positions are shown by black vertical bars. As seen, all the XRD peaks could be indexed as 1/1 AP indicating that this phase is formed inside a relatively elongated compositional area up to ~ 20 at% Mg. A complete set of measured and refined XRD spectra for all samples are provided separately as a supplementary material (<https://stacks.iop.org/JPCM/32/485801/mmedia>). The variation of the lattice parameter as a function of analyzed Mg content of the prepared alloys is displayed in figure 4. Clearly, the lattice parameter increases from 15.4842(5) Å in Cd_{81.26}Mg_{4.18}Tb_{14.56} to 15.5104(4) Å in Cd_{64.09}Mg_{21.34}Tb_{14.57}. This is due to the slightly larger atomic radius of Mg (1.60 Å) compared to that of Cd (1.57 Å) [25] leading to expansion of the unit cell, as expected from Vegard's law. However, the unit

**Figure 4.** Variation of lattice parameters of the cubic 1/1 APs as a function of their constituent Mg content obtained using Le Bail analysis. Here we used the analyzed Mg composition obtained from SEM–EDX experiment. The sudden jump of the lattice parameters above ~ 12 at% Mg might be correlated with the filling up of some preferred atomic sites by Mg.**Figure 5.** (a) Temperature dependence of DC magnetic susceptibility of the Cd₆₅Mg₂₀Tb₁₅ 1/1 AP measured under $H = 100$ Oe in the temperature range of 2–300 K showing both FC and ZFC behaviors. Open and close circles represent FC and ZFC curves, respectively. The inset shows the inverse susceptibility of the same alloy. (b) Magnified low-temperature DC magnetic susceptibilities of the 1/1 APs containing 5, 10, 15 and 20 at% Mg in Cd–Mg–Tb system.

cell expansion does not follow a monotonous trend; it grows gradually up to about 12 at% Mg, above which it undergoes a swift expansion. The lattice parameter growth seems to saturate when the Mg content approaches the solubility limit in 1/1 AP (i.e. ~ 20 at% Mg). A slight deviation of the lattice parameter of the sample with 7.5 at% Mg from a linear trend may be attributed to an error originating from SEM–EDX elemental analysis. A sudden rise of the lattice parameters above ~ 12 at% Mg, however, might be correlated with the filling up of some preferred atomic sites by Mg, which will be discussed in detail later.

Figure 5(a) depicts the temperature dependence of DC magnetic susceptibility for the Cd₆₅Mg₂₀Tb₁₅ 1/1 AP, as a typical example, measured under 100 Oe in a temperature range of 2–300 K. Measured susceptibility data under the FC and ZFC conditions are shown with open and filled circles, respectively. The corresponding inverse magnetic susceptibility data shown in the inset fit well with the Curie–Weiss law in a high

Table 2. Weiss temperature (Θ_w), the freezing temperatures (T_{f1} , T_{f2}), and effective magnetic moment (μ_{eff}) of the $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 10, 15$ and 20) 1/1 APs. Appearance of successive phase transitions is associated with the existence of various AFM magnetic configurations, which are nearly degenerate, over a bcc array of icosahedral clusters.

Nominal composition	μ_{eff} ($\mu_B/\text{RE}_{\text{ion}}$)	$\mu_{\text{calc.}}$ ($\mu_B/\text{RE}_{\text{ion}}$)	Θ_w (K)	T_{f1} (K)	T_{f2} (K)	T_N (K)
$\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$	9.6 ± 0.2		-14 ± 2	3.0 ± 0.5	—	20.5 ± 0.5
$\text{Cd}_{75}\text{Mg}_{10}\text{Tb}_{15}$	9.8 ± 0.2	9.72	-14 ± 2	3.0 ± 0.5	17.0 ± 0.5^a	
$\text{Cd}_{70}\text{Mg}_{15}\text{Tb}_{15}$	9.4 ± 0.2		-16 ± 2	3.0 ± 0.5	17.0 ± 0.5^a	
$\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$	9.4 ± 0.2		-18 ± 2	3.0 ± 0.5	13.5 ± 0.5	—

^aThe boxes highlighted in gray to represent an uncertainty in assigning the anomalies to the T_{f2} or T_N .

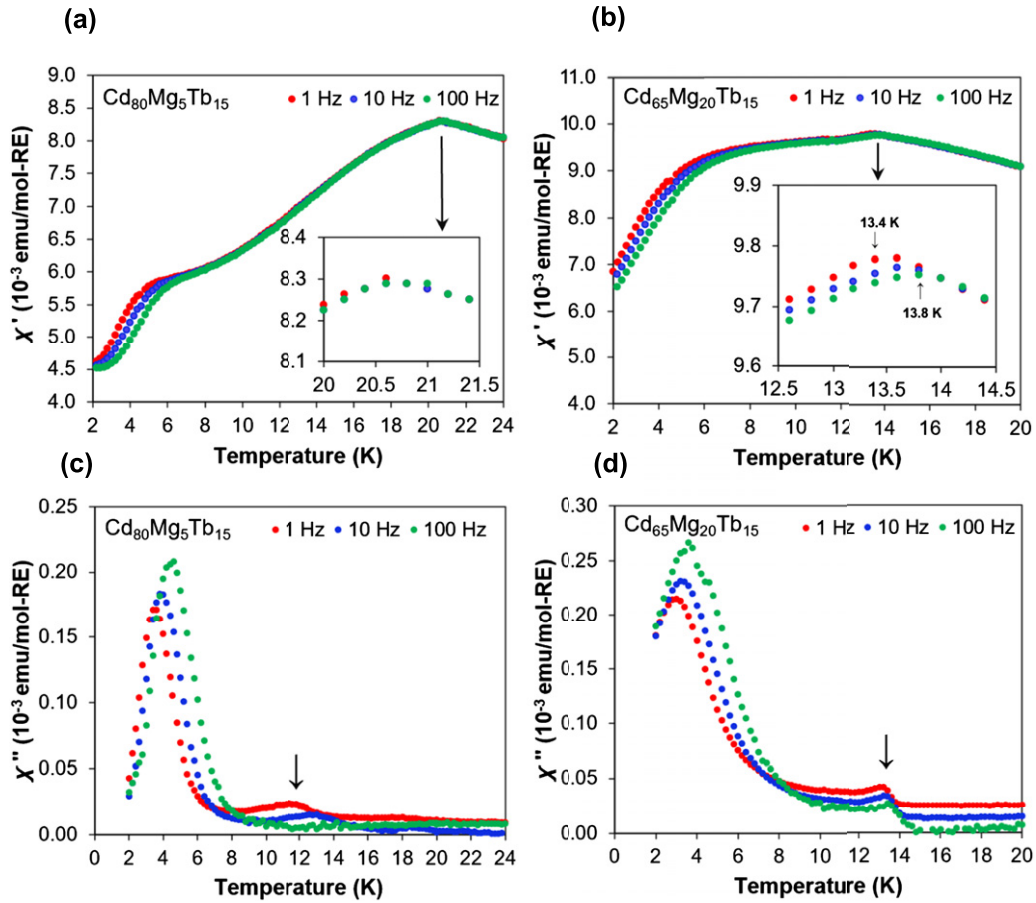


Figure 6. The in-phase and out-of-phase components of the AC susceptibilities for the (a) and (c) $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ and (b) and (d) $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ measured under $f_{\text{AC}} = 1\text{--}100$ Hz. The insets in figures 5(a) and (b) show the magnified view of the susceptibility curves around the cusp.

temperature region ($100\text{ K} < T < 300\text{ K}$):

$$\chi(T) = \frac{N_A \mu_{\text{eff}}^2}{3k_B (T - \theta_w)} + \chi_0 \quad (1)$$

where N_A , k_B , μ_B and χ_0 stand for Avogadro's number, the Boltzmann factor, Bohr magneton and the temperature-independent magnetic susceptibility, respectively. The χ_0 is approximately zero in the present samples. The Weiss temperature, θ_w , and the effective magnetic moment, μ_{eff} , are estimated for each of the four compounds by linear least-squares fitting of their inverse susceptibility data to the Curie–Weiss law and extrapolating the fitting data to the temperature axis. Table 2 lists the estimated μ_{eff} , θ_w , and T_f or T_N for samples

possessing 5, 10, 15, 20 at% Mg (nominal). The measured θ_w values are negative demonstrating AFM interactions between the magnetic moments. The given uncertainty of ± 2 K in the estimation of θ_w in table 2 corresponds to the standard deviation from a mean value after averaging the obtained θ_w by fitting over different temperature ranges within 100–300 K (with 50 K intervals). The μ_{eff} values are consistent with the ideal values calculated for the Tb^{3+} free ion, i.e. $9.72 \mu_B$, confirming that Tb ions are trivalent.

A magnetic phase transition temperature, at which an anomaly associated either with magnetic freezing (T_f) or AFM ordering (T_N) occurred, was determined from the magnified low-temperature DC susceptibility curves shown in figure 5(b). The figure clearly evidences the occurrence of two

anomalies in each of the susceptibility curves for the 1/1 APs containing 5, 10, 15 and 20 at% Mg in Cd–Mg–Tb system. In $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$, for instance, both χ_{ZFC} and χ_{FC} curves are peaked at $T \sim 21$ K, while at $T \sim 3$ K only ZFC shows a maximum. The onset of the bifurcation between ZFC and FC data occurs at $T \sim 12$ K. The susceptibility curve of $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ exhibits similar features to that of $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ except the maximum of ZFC data that appears at $T \sim 13$ K. Below $T \sim 13$ K, the bifurcation between ZFC and FC magnetization curves takes place. Such a bifurcation points to an SG-like freezing transition [26]. The transition temperatures for $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 10, 15$ and 20) compounds are listed in table 2.

Figure 6 depicts in-phase (χ'_{AC}) and out-of-phase (χ''_{AC}) components of the AC magnetic susceptibilities for the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ and $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ alloys under selected frequencies between 1 to 100 Hz. The insets in figures 6(a) and (b) provide magnified views of the susceptibility curves around the cusps. The cusps in χ''_{AC} curves are noticed at exactly the same temperatures as those observed in the DC magnetization curves in figure 4(b). As seen from the insets, the amplitude and position of the cusp in the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ alloy (figure 6(a), at around 21 K) are independent of the frequency of the applied field, whereas they are systematically affected by the frequency variation in the $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ alloy (figure 6(b), at around 13–14 K). At $T \sim 3$ K, however, both alloys exhibit frequency-dependent variation of the χ'_{AC} . These results confirm that the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ alloy undergoes an AFM ordering and SG-like freezing at $T \sim 21$ and 3 K, respectively. This is consistent with the earlier reports about the binary Cd_6Tb where the partial participation of Tb moments in the AFM ordering at $T = 24$ K and the SG freezing of the rest at lower temperature is reported [11, 15, 16, 27–29]. The out-of-phase components χ''_{AC} evidence the occurrence of two frequency dependent peaks for both alloys: the strong peaks at $T \sim 3$ K followed by weak peaks at $T \sim 12$ –13 K (indicated by arrows in figures 6(c) and (d)). The weak peak at $T \sim 12$ K for $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$, which disappears with the frequency increment, might reflect either a certain, yet unclarified slow spin dynamics or possible impurities within the samples. Note that all investigated samples exhibit such weak peaks at $T \sim 12$ –13 K. The $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ alloy, on the other hand, exhibits two successive SG-like transitions at $T \sim 3$ and 13.5 K. This implies that the Mg substitution to the Cd_6Tb 1/1 AP structure (shown in figure 1) disrupts the long-ranged AFM ordering and induces the SG-like transition above the threshold Mg concentration of ~ 12 –14 at%.

In order to gain further insights into the AFM to SG-like magnetic transition from the viewpoint of the crystal structure, TEM experiments have been carried out. Figure 7 presents the selected area electron diffraction (SAED) patterns of the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ and $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ 1/1 APs taken with an incidence along $[111]_{\text{C}}$ (subscript C denotes a cubic lattice) at $T = 100$ K and 300 K. While the SAED pattern of $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ at $T = 100$ K exhibits superlattice reflections at the midpoints of the fundamental reflections, as marked with red arrowheads in figure 7(a), that of the same sample at $T = 300$ K shows no superlattice reflections (see figure 7(b)). The superlattice

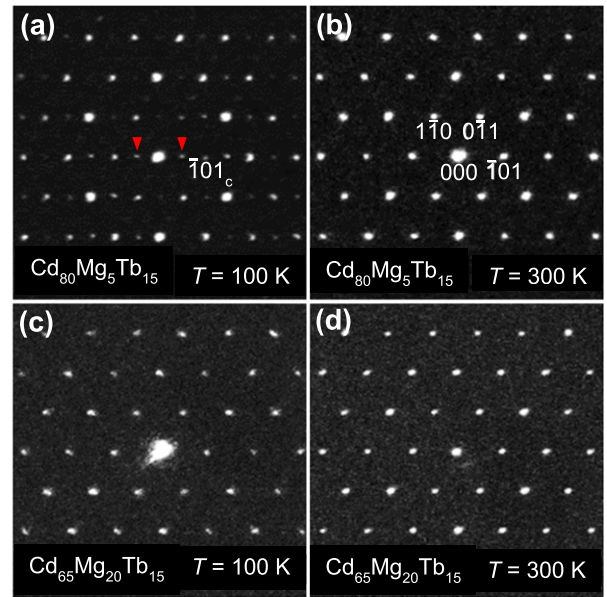


Figure 7. SAED patterns taken with an incidence along $[111]_{\text{C}}$ of the (a) and (b) $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ and (c) and (d) $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ at 100 K and 300 K. The superlattice reflections are found in the pattern of the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ at 100 K, as indicated by arrow heads.

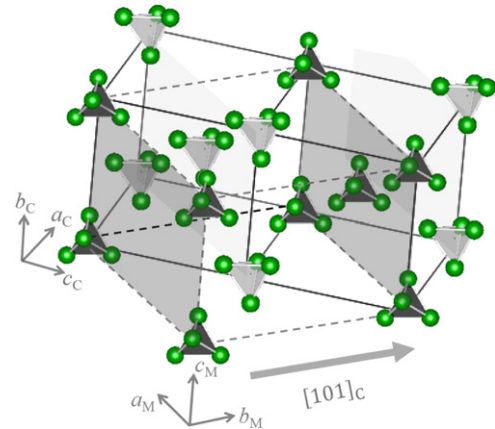


Figure 8. Schematic illustration of the possible low-temperature superstructure of $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ regarding the orientation of the Cd_4 tetrahedron at the center of the each RTH cluster. Planes with different colors represent different orientations of the Cd_4 tetrahedron. ($a_{\text{C}}, b_{\text{C}}, c_{\text{C}}$) and ($a_{\text{M}}, b_{\text{M}}, c_{\text{M}}$) stand for a cubic and monoclinic lattice basic vectors, respectively.

reflections in figure 7(a) indicate the doubling of the periodicity along $[101]_{\text{C}}$, clearly breaking the threefold symmetry. This means that a structural phase transition has occurred in the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ during cooling. In fact, similar phenomena have been commonly observed in the binary Cd_6RE and Zn_6Sc 1/1 APs, and have been described as order–disorder-type phase transitions associated with the orientations of the Cd_4 tetrahedra. Here, the low temperature phase takes a monoclinic structure [11, 15, 28, 30–33]. In the binary systems, the transition temperature depends on the RE type, but is always in the range of $100 < T < 200$ K [30, 31, 34]. Figure 8 presents a schematic illustration of the low-temperature superstructure of the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ 1/1 APs with respect to orientational

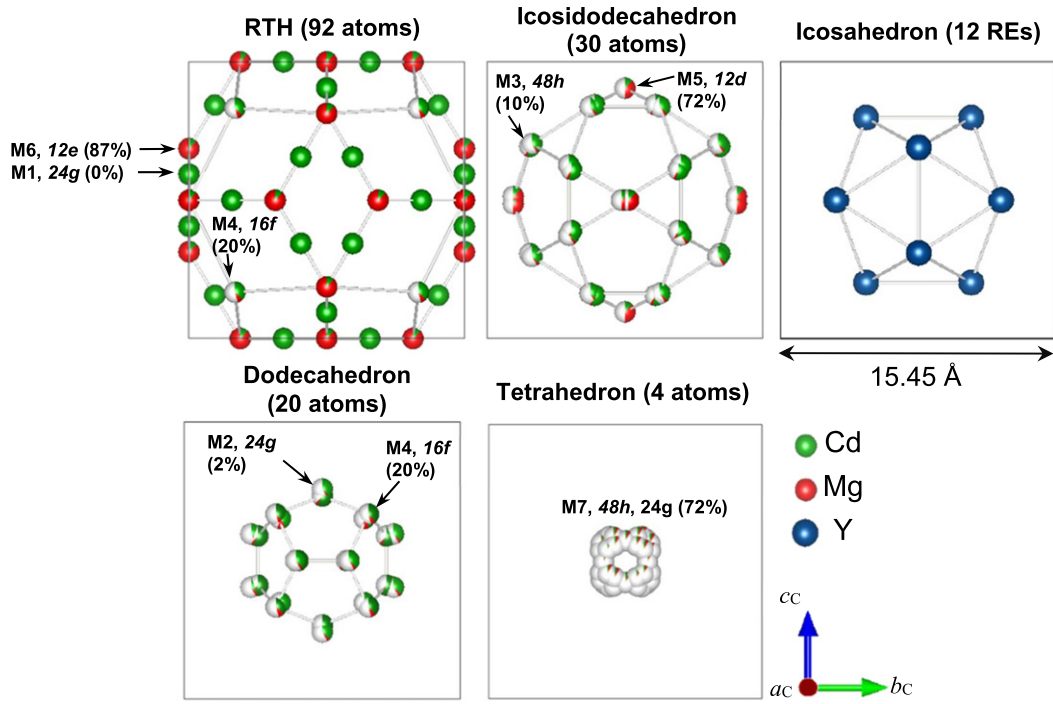


Figure 9. The successive sequence of atomic shells in the $\text{Cd}_{65}\text{Mg}_{20}\text{Y}_{15}$ 1/1 AP. Occurrence of 60 atoms in the central tetrahedron is due to the two types of disorders: a 90° rotational disorder along its 2-fold axis and a triple splitting of the tetrahedral corner positions. The lattice parameter is 15.45 Å. The numbers in parentheses refer to Mg occupational fraction.

ordering of the Cd_4 tetrahedra. In the figure, planes with different colors represent different orientations of the Cd_4 tetrahedron. Solid lines indicate cubic unit cells for the high-temperature phase, while dashed lines show a monoclinic unit cell for the low-temperature phase. Interestingly, the SAED patterns of the $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ 1/1 AP at both $T = 100$ and 300 K (figures 7(c) and (d)) show no superlattice reflections down to low temperatures indicating that, unlike $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$, the crystal remains disordered in terms of the orientations of the Cd_4 tetrahedra. The absence of the ordering in the orientations of the tetrahedra might possibly explain why $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ exhibits no AFM ordering but only SG-like transition at low temperatures (see figures 5 and 6). To the best of our knowledge, this is the first observation that indicates that a high Mg content hinders the ordering of central Cd_4 tetrahedra and further long-ranged AFM ordering in 1/1 AP.

One possible factor that hinders the orientational ordering of Cd_4 tetrahedron in alloys with high Mg content may be the effect of Mg atoms that enters into the central tetrahedral shell. Based on the only structure analysis in hand, i.e. the structure of the $\text{Cd}_{65}\text{Mg}_{20}\text{Y}_{15}$ 1/1 AP shown in figure 9 [35], the three most preferred Mg occupational sites are the vertex positions of the RTH (M6 sites), the positions on the two-fold axes of the icosidodecahedron (M5 sites) and the central tetrahedron (M7 sites), with 87%, 72% and 72% occupational fractions of Mg, respectively. The M6 sites, in particular, shows a relatively strong tendency to accept Mg. The numbers in parentheses in figure 9 refer to Mg occupational fractions. It is instructive to note that the Mg content that resides on the M6 sites alone amounts to 12.42 at% in the total composition. The latter value is reasonably close to the threshold Mg concentration in

figure 4 above which the lattice parameters rise significantly (i.e. ~ 12 at%). This suggests a possible scenario that upon increasing the Mg content, most Mg atoms would first go into the M6 sites if the Mg content is low, while if Mg content exceeds ~ 12 at%, Mg atoms would start to occupy the other sites including those in the central tetrahedra, inhibiting the ordering of their orientations. This picture needs to be further verified through more detailed analyses, which is left for future studies.

Another important factor to consider when discussing the order-disorder transition in 1/1 APs in the course of increasing Mg content is the size effect of the second shell dodecahedra that encage the central tetrahedra. It has been commonly assumed that too short interatomic distances between the central tetrahedron and the surrounding dodecahedron would induce a deformation of the dodecahedral shell thus costing elastic strain energy, while the ordering would take place to minimize the energy [30, 36]. At high-enough temperatures, the entropy gain could compensate for the energy cost. Using the Helmholtz formula, the differential free energy ΔF upon disordering can be written as $\Delta F = \Delta E - T\Delta S$, where $\Delta E (>0)$ and $\Delta S (>0)$ denote the energy and entropy differences, respectively, (i.e. $\Delta E = E_{\text{disordered}} - E_{\text{ordered}}$, $\Delta S = S_{\text{disordered}} - S_{\text{ordered}}$) at temperature T . As a crude approximation, one can assume that ΔS is a constant. Then the transition temperature T_c , which follows from $\Delta F = \Delta E - T_c\Delta S = 0$, scales linearly with ΔE . Importantly, as the lattice parameter increases, the volume of the dodecahedron expands and the distances between the neighboring atoms located on the tetrahedron and the dodecahedron increases, which leads to lower strain energy and thus lower ΔE . For Cd_6RE 1/1 APs

having larger RE atoms and thus a larger volume of the dodecahedron, the transition temperature is reported to be relatively lower than those with smaller RE size [30, 36]. The present argument is fully consistent with this observation, and can also be naturally extended to the present system of ternary alloys. Note that the dodecahedron volume increases following the significant rise in the lattice parameter of 1/1 APs above ~ 12 at% Mg (see figure 4) leading the structural transition temperature (T_c) to drop. In this scenario, the structural transition in $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ 1/1 AP (nominal composition) may still take place below $T = 100$ K. However, the probability of the tetrahedron reorientation is proportional to $\exp(-E_a/k_B T)$, where the E_a and k_B are the activation energy of the tetrahedron reorientation and the Boltzmann factor, respectively [30, 36]. In this sense, the reorientation of the tetrahedron (disordering) is strongly dependent on the temperature and might be kinetically frozen at lower temperatures.

Here, the underlying reasons of the composition-driven AFM to SG-like magnetic transition will be discussed. The composition-dependent AFM to FM and FM to SG transitions have been reported in the Au–Al–RE (RE = Gd and Tb) systems [27, 37] and been interpreted by the impact of Au/Al variation on the electron-per-atom (e/a) ratio of the compounds. However, given that both Mg and Cd are divalent, the e/a values of the present $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 10, 15, 20$) compounds equal 2.15. Therefore, the AFM to SG-like magnetic transition in the present study is perhaps not triggered by e/a ratio, but rather by the suppression of Cd_4 tetrahedra ordering, which is a key element in the establishment of AFM magnetic transition. Indeed, the cubic to monoclinic structural transition induces a strong distortion which plays an important role in relieving some degree of magnetic frustration inherent to the RE elements with nearly perfect icosahedral arrangement in the cubic structure and favors the occurrence of AFM magnetic transition [28]. Nevertheless, the structural disorder of inner Cd_4 tetrahedron may induce randomness of crystal electric field (CEF) and raise the SG-like freezing of the RE magnetic moments at low temperatures. The present result calls for further experimental and theoretical studies for more clarification.

Note that the chemical disorder of the Cd/Mg should also be taken into account as the source of disorder contributing to the observed SG behavior in alloys with high Mg content. The importance of chemical disorder was recently confirmed by measuring CEF splitting in Au–Si–Tb 1/1 AP [38]. It seems reasonable, therefore, to assume that the combination of chemical disorder due to a randomized substitution of Cd with Mg and the orientational disorder of the Cd_4 tetrahedra is responsible for the occurrence of the AFM to SG-like magnetic transition in the present compounds.

4. Conclusion

This research was undertaken to evaluate the effect of Mg/Cd substitution on the crystal structure and magnetic properties in the $\text{Cd}_{85-x}\text{Mg}_x\text{Tb}_{15}$ ($x = 5, 10, 15, 20$) 1/1 APs. Each of the four compounds exhibited two anomalies in their DC magnetic susceptibilities. The higher transition temperature was

found to be of the AFM-type in the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ and SG-type in the $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$. The superlattice reflections were observed in the SAED pattern of the $\text{Cd}_{80}\text{Mg}_5\text{Tb}_{15}$ at $T = 100$ K, whereas no superlattice reflections were noticed for the $\text{Cd}_{65}\text{Mg}_{20}\text{Tb}_{15}$ at the same temperature. The appearance of superlattice reflections is associated with the order-disorder-type phase transition with respect to the orientations of the Cd_4 tetrahedra. Taken together, the combined effect of chemical disorder of Cd/Mg and orientational disorder of the Cd_4 tetrahedra is presumably responsible for the occurrence of the AFM to SG-like magnetic transition in the present compounds.

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