We report magnetic properties of Cd₆RE (RE= Tb, Sm) single-grained crystalline approximants. Magnetic susceptibilities show that various long-range magnetic orders occur at low temperatures for the compounds made of RE icosahedra: Cd₆Tb shows three types of antiferromagnetic orders with temperature and Cd₆Sm exhibits also three types of magnetic orders with temperature, i.e., one antiferromagnetic and two types of ferrimagnetic orders.

Key words: Rare-Earth Compounds, Quasicrystalline Approximants, Magnetic Properties

1. INTRODUCTION

Quasicrystals[1] are known as aperiodic solids that lack translational symmetry but have rotational symmetries forbidden in crystals, i.e., fivefold, eightfold, tenfold and 12-fold rotational symmetries. Until now, a number of quasicrystals have been discovered over 70 alloy systems. However, because of the existence of chemical disorder which are thought to obscure “quasiperiodicity”, it has been difficult to understand the structural and physical properties intrinsic to quasicrystals. In this respect, the Cd-based binary quasicrystals Cd₅.₇Ca[2] and Cd₅.₇Yb[3] which were discovered by Tsai et.al. in 2000 have helped us to study the structural and physical properties of quasicrystals since they have no chemical disorder. For an instance, the first successful structural analysis was performed in Cd₅.₇Yb[4].

Amongst various physical properties of quasicrystals, the magnetic properties of quasicrystals containing 4f rare earth elements have caught much attention. Magnetic measurements on the Cd(Zn)-Mg-RE (RE= rare earth elements) quasicrystals have been performed systematically, which has shown spin glass-like behaviors of localized RE³⁺ spins at low temperature in all the cases, however, no long-range magnetic states has been reported[5,6,7].

Meanwhile, crystalline approximants are also of significant interest since they allow us to understand the structural and physical properties of the quasicrystals with respect to the common local structure. The Cd₆M (M = Ca, Y, Rare earth elements) compounds, body-centered-cubic (bcc) crystals with space group Im-3 and a ~ 1.5 nm[8], are known as crystalline approximants to the Cd₅.₇Ca and Cd₅.₇Yb icosahedral quasicrystals. According to the single crystal structural analyses[9,10], the Cd₆M compounds contain 168 atoms in a unit cell and consists of four successive shells (called Tsai-type cluster, see Figure 1(a), i.e., from the cluster center, a Cd₄ tetrahedron, a Cd₂₀ dodecahedron, a M₁₂ icosahedron and a Cd₃₀ icosidodecahedron, together with “glue” Cd atoms which fill the space in between the clusters. It is noted that M atoms occupy the icosahedral (24g) site without chemical or positional disorder. The systems can also be regarded as new 4f spin systems that are composed of icosahedral RE₁₂ clusters (See Figure1 (b)).

In this article, we report results of magnetic property measurements on Cd₆Tb and Cd₆Sm as typical examples.
and discuss their magnetic properties as well as their long-range magnetic orders at low temperatures.

2. EXPERIMENTAL PROCEDURES

Single grains of Cd₆RE (RE = Tb, Sm) approximants were prepared by a self-flux growth technique. Pure elements of the starting composition of Cd(6N):RE(3N) = 9:1 were placed inside an alumina crucible sealed inside a quartz tube under Argon atmosphere. The raw materials were melted at 993 K for 24 h, and slowly cooled at the rate of -2 K/h to 773 K. At 773 K, the crucible was taken out from the muffle furnace and the Cd melt was rapidly decanted by turning the crucible upside down and centrifuging using a high-speed centrifuge. The obtained single grains exhibit well defined facets surrounded by \{100\} and \{110\} planes. Single grains were subsequently annealed in order to improve the sample homogeneity as well as to reduce point defects. The magnetic properties were measured from 1.8 to 300 K by using a SQUID magnetometer (Quantum Design, MPMS) under 50 or 1000 Oe.

3. RESULTS AND DISCUSSION

3.1 Magnetic properties at high temperatures

Figures 2(a) and (b) show the magnetic susceptibility \( \chi \) and the inversed magnetic susceptibility \( 1/\chi \) as a function of temperature measured from 2 to 300 K for Cd₆Tb and Cd₆Sm approximants, respectively. The susceptibility of Cd₆Tb above 50 K obeys the Curie-Weiss law,

\[
\chi(T) = \frac{N_A \mu_{eff}^2}{3k_\text{B}(T-\Theta)}
\]

Avogadro’s number, \( \mu_{eff} \) is the effective magnetic moment, \( k_\text{B} \) is the Boltzmann’s constant and \( \Theta \) is the Curie-Weiss temperature, respectively. On the other hand, the magnetic susceptibility of Cd₆Sm (Figure 2(b)) does not obey the Curie-Weiss law, most likely because of the small energy difference between the Hund’s rule ground state (\( J=5/2 \)) and the first excited state (\( J=7/2 \))[11]. Therefore, the susceptibility data of Cd₆Sm were fitted by a following formula which incorporates a temperature-independent Van Vleck term due to the thermal excitation of first excited state into the Curie-Weiss law,

\[
\chi(T) = \left[ \frac{N_A}{k_\text{B}} \right] \left( \frac{\mu_{eff}^2}{3(T-\Theta)} + \frac{\mu_\text{B}^2}{\delta} \right)
\]

where, \( \mu_\text{B} \) is the Bohr magneton and \( \delta = 7\Delta/20 \) where \( \Delta \) is the energy difference in units of Kelvin between the \( J=5/2 \) and \( J=7/2 \) multiplet states[12]. Table 1 shows the parameters obtained by the least square fits to the magnetic susceptibilities of Cd₆Tb and Cd₆Sm. The negative \( \Theta \) values in both systems mean that major interaction between 4\( f \) spins are antiferromagnetic in the paramagnetic state. The values of effective magnetic moments are approximately the same as those of free RE\(^{3+} \) ions, which suggests that RE\(^{3+} \) atoms are well localized at the vertices of the RE\(_{12} \) icosahedron, hardly affected by crystalline-field splitting effect.

3.2 Magnetic orders at low temperatures

Figures 3(a) and (b) show low-temperature magnetic susceptibility as a function of temperature from 1.8 to 30 K for Cd₆Tb and Cd₆Sm approximants, respectively. The susceptibility of Cd₆Tb exhibits three successive anomalies at 1.9, 19.0 and 24.0 K which are interpreted as antiferromagnetic transitions. The result is consistent with those on a poly-grain sample recently reported by Tamura et. al.[13] The Cd₆Sm approximant also exhibits three successive magnetic transitions with temperature, i.e., an antiferromagnetic one (12.5 K) and two ferrimagnetic ones (10.0 and 6.5 K). For both

<table>
<thead>
<tr>
<th>Θ / K</th>
<th>Cd₆Tb</th>
<th>Cd₆Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{eff} / \mu_\text{B} )</td>
<td>9.95</td>
<td>0.59</td>
</tr>
<tr>
<td>( \mu_{\text{theol}} / \mu_\text{B} )</td>
<td>9.72</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 1. Weiss temperature Θ and effective magnetic moments \( \mu_{eff} \) of Cd₆Tb and Cd₆Sm. For a comparison, the magnitude of the theoretical RE\(^{3+} \) moments (\( \mu_{\text{theol}} \)) are also shown.
systems, specific heat also displays anomalies and/or peaks at the transition temperatures (not shown) indicating that the successive transitions are due to long-range magnetic orders. These results in Cd₆RE are different from the spin glass-like behaviors observed in, for instance, Ag-In-RE approximants [14]. The present work clearly shows that long-range magnetic orders are allowed for ⁴f magnetic moments sitting on the vertices of an icosahedron.

4. CONCLUSION

We have measured magnetic properties of Cd₆RE (RE= Tb, Sm) single-grained crystalline approximants. Above 50 K, the magnetic susceptibility of Cd₆Tb obeys the Curie-Weiss law whereas that of Cd₆Sm does not follow the law but is explained by including the contribution from the van Vleck term. The obtained effective magnetic moments suggest that RE³⁺ atoms are well localized in a trivalent state at the vertices of the RE₁₂ icosahedron. At low temperatures, both the approximants exhibit successive magnetic transitions, i.e., antiferro- and/or ferri- magnetic orders, below 30 K. These results are different from the observations in other quasicrystals and approximants which exclusively show spin glass-like behaviors.

5. REFERENCES


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