Magnetic Orders in Compounds Made of Icosahedral Rare-Earth Clusters

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We report magnetic properties of Cd_6RE (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: Cd_6Tb shows three types of antiferromagnetic orders with temperature and Cd_6Sm 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 $\text{Cd}_{5.7}\text{Ca}$ ^[2] and $\text{Cd}_{5.7}\text{Yb}$ ^[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 $\text{Cd}_{5.7}\text{Yb}$ ^[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 RE^{3+} 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 Cd_6M (M = Ca, Y, Rare earth elements) compounds, body-centered-cubic (bcc) crystals with space group $\text{Im}-3$ and $a \sim 1.5 \text{ nm}$ ^[8], are known as crystalline approximants to the $\text{Cd}_{5.7}\text{Ca}$ and $\text{Cd}_{5.7}\text{Yb}$ icosahedral

quasicrystals. According to the single crystal structural analyses^[9,10], the Cd_6M 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 Cd_4 tetrahedron, a Cd_{20} dodecahedron, a M_{12} icosahedron and a Cd_{30} 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 RE_{12} clusters (See Figure 1(b)).

In this article, we report results of magnetic property measurements on Cd_6Tb and Cd_6Sm as typical examples

Figure1. (a) Tsai-type cluster and (b) bcc packing of RE_{12} icosahedra in Cd_6RE cubic approximants.

and discuss their magnetic properties as well as their long-range magnetic orders at low temperatures.

2. EXPERIMENTAL PROCEDURES

Single grains of Cd_6RE (RE = Tb, Sm) approximants were prepared by a self-flux growth technique. Pure elements of the starting composition of $\text{Cd}(6\text{N}):\text{RE}(3\text{N}) = 9:1$ 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 magnet meter (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 χ and the inversed magnetic susceptibility $1/\chi$ as a function of temperature measured from 2 to 300 K for Cd_6Tb and Cd_6Sm approximants, respectively. The susceptibility of Cd_6Tb above 50 K obeys the Curie-Weiss law, $\chi(T) = \frac{N_A \mu_{\text{eff}}^2}{3k_B(T - \theta)}$, where, N_A is the

Avogadro's number, μ_{eff} is the effective magnetic moment, k_B is the Boltzmann's constant and θ is the Curie-Weiss temperature, respectively. On the other hand, the magnetic susceptibility of Cd_6Sm (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 Cd_6Sm 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, $\chi(T) = \left(\frac{N_A}{k_B} \right) \left[\frac{\mu_{\text{eff}}^2}{3(T - \theta)} + \frac{\mu_B}{\delta} \right]$, where,

μ_B is the Bohr magneton and $\delta = 7\Delta/20$ where Δ 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 Cd_6Tb and Cd_6Sm . The negative θ values in both systems mean that major interaction between $4f$ 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

Figure 2. Magnetic susceptibility (open circle) and inversed susceptibility (open triangle) of (a) Cd_6Tb and (b) Cd_6Sm approximants measured in a field of 1000 Oe

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 Cd_6Tb and Cd_6Sm approximants, respectively. The susceptibility of Cd_6Tb 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 Cd_6Sm 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 1. Weiss temperature θ and effective magnetic moments μ_{eff} of Cd_6Tb and Cd_6Sm . For a comparison, the magnitude of the theoretical RE^{3+} moments ($\mu_{\text{theor.}}$) are also shown.

	Cd_6Tb	Cd_6Sm
θ / K	-17.5	-16
μ_{eff} / μ_B	9.95	0.59
$\mu_{\text{theor.}} / \mu_B$	9.72	0.85

Figure 3. Low temperature magnetic susceptibility of (a) Cd_6Tb and (b) Cd_6Sm . Cd_6Tb was measured at zero-field cooled (ZFC) and field cooled (FC) under 50 Oe. Cd_6Sm was measured under 1000 Oe.

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 Cd_6RE 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 Cd_6RE (RE= Tb, Sm) single-grained crystalline approximants. Above 50 K, the magnetic susceptibility of Cd_6Tb obeys the Curie-Weiss law whereas that of Cd_6Sm does not follow the law but is explained by including the contribution from the van Vleck term. The obtained effective magnetic moments suggest that RE^{3+} atoms are well localized in a trivalent state at the vertices of the RE_{12} 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.

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