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LETTER TO THE EDITOR

Magnetic properties of the icosahedral Cd–Mg–rare-earth quasicrystals

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Abstract

We report dc and ac magnetization of the newly discovered Cd–Mg–RE quasicrystals (RE = Gd, Tb, Dy, Ho, Er, Tm and Yb). For all the RE atoms except Yb, the temperature dependence of the dc magnetization obeys the Curie–Weiss law at higher temperatures, $T > 50$ K. Estimated effective moments indicate that these atoms are in the trivalent states. In contrast, the Cd–Mg–Yb quasicrystal shows very small magnetization, suggesting that Yb is in the non-magnetic divalent state. At lower temperatures, spin–glass-like freezing was observed for the RE atoms except Tm and Yb. In particular, the freezing proceeds in two successive steps for RE = Gd, Tb, Dy and Ho, being quite different from canonical spin–glasses.

1. Introduction

Since the discovery of quasicrystals, the behaviour of spin systems in quasiperiodic structure has been of particular interest. To study the behaviour experimentally, it is necessary to find quasicrystals with well-localized magnetic moments. Until recently, only the Zn–Mg–RE (RE = Gd, Tb, Dy, Ho and Er) icosahedral quasicrystals came into this class [1], and thus have been intensively investigated [2–7]. The results can be briefly summarized as follows. The temperature dependence of the magnetic susceptibility shows the Curie–Weiss behaviour at higher temperatures. Estimated effective magnetic moments correspond to those of free RE^{3+} ions, confirming the well-localized moments originating from 4f electrons of the RE atoms. At lower temperatures of about a few Kelvin, the Zn–Mg–RE quasicrystals exhibit spin–glass-like freezing, similar to canonical spin–glasses [8]. In the spin–glass-like state, however, neutron scattering detected novel short-range-spin correlations described by a six-dimensional modulation vector [9].

Quite recently, Guo *et al* have found icosahedral quasicrystals in the Cd–Mg–RE (RE = Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) alloys [10]. They are thermodynamically

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stable, and have a primitive icosahedral lattice. The Cd–Mg–RE quasicrystals are the second example of quasicrystals including RE atoms, in which the formation of localized moments is highly expected. Therefore, it now becomes possible to compare the behaviour of the localized moments in the two different systems. This may clarify universal properties of the localized moments in icosahedral quasicrystals. In addition, the Cd–Mg–RE quasicrystals can be obtained for RE = Tm and Yb, for which so-called valence-fluctuation phenomena are sometimes observed in crystalline materials [11]. Thus, the Cd–Mg–RE quasicrystals provide a first opportunity to study electronic and magnetic states of such RE atoms in the quasicrystalline structure.

In this study, we measured the dc and ac magnetization of the Cd–Mg–RE quasicrystals as a first attempt to reveal their macroscopic magnetic properties. For the magnetic measurements, one has to obtain quasicrystalline samples in which magnetically contaminating crystalline phases are completely eliminated. Therefore, we also carried out a metallographic survey for the samples.

2. Sample preparation

As-cast alloys were prepared by melting constituent elements in an induction furnace under an Ar gas atmosphere using high purity Al_2O_3 crucibles. Purities of the starting elements were 99.9999 wt.%, 99.99 wt.% and 99.9 wt.% for Cd, Mg and RE, respectively. Parts of the alloys were wrapped in Ta foils, sealed in Pyrex or quartz tubes, and annealed at elevated temperatures. Microstructures of the alloys were checked using a scanning electron microscope (SEM), and their compositions were determined by energy dispersive x-ray spectroscopy with pure elements as standards. The crystal structure was checked by x-ray powder and electron diffraction.

Following the work of Guo *et al* [10], we prepared the $Cd_{65}Mg_{20}RE_{15}$ alloys annealed at 673 K for 250 h. The alloys mostly consist of the quasicrystalline phase for RE = Tm and Yb, and thus were used in the following magnetic measurements. However, for the other RE elements, the resulting alloys were contaminated by the crystalline $Cd_{80-x}Mg_xRE_{20}$

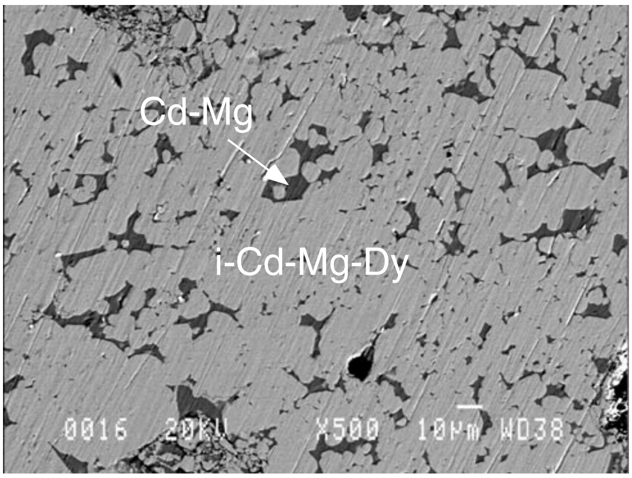

Figure 1. The backscattering electron image of the $Cd_{55}Mg_{35}Dy_{10}$ alloy annealed at 723 K for 100 h, taken in the SEM.

($x \sim 20$) phase, because the equilibrium RE concentration of the quasicrystalline phase is slightly lower than 15%. The crystalline phase contains a large amount of RE atoms, and thus may possibly smear magnetic signals from the quasicrystalline phase. Therefore, we reduced the RE concentration to completely eliminate the ternary crystalline phase for those RE alloys. The backscattering electron image of the $Cd_{55}Mg_{35}Dy_{10}$ alloy annealed at 723 K for 100 h is shown in figure 1. The dominant phase is the quasicrystalline phase, whereas a very small amount of the Cd–Mg binary phase can be seen. No ternary crystalline phase was detected. Since the binary phase is non-magnetic, it will not affect the magnetic measurements. Similar results were obtained for the Gd, Tb, Ho and Er alloys. Thus, for RE = Gd, Tb, Dy, Ho and Er, the $Cd_{55}Mg_{35}RE_{10}$ alloys were used in the magnetic measurements. We could not find any good conditions for RE = Nd and Eu, so that these quasicrystals were not investigated. It should be noted that the composition of the quasicrystalline phase is about $Cd_{60}Mg_{28}RE_{13}$ with small deviations depending on the RE atoms. Nevertheless, we used the nominal composition in the following analysis; the samples were homogeneous mixtures of the quasicrystalline and binary phases, and thus should have the nominal composition on average.

3. Results and discussion

Both dc and ac magnetization were measured using a superconducting quantum interfering device (SQUID) magnetometer (MPMS-XL, Quantum Design). The temperature dependence of the dc magnetization was measured for $2 < T < 300$ K under several external fields. Both field-cooled (FC) and zero-field-cooled (ZFC) procedures were employed. Some of the results are presented using magnetic susceptibility χ_{dc}, which is defined as $\chi_{dc} = M/H$ for the low-field measurements. The ac magnetic susceptibility χ_{ac} was measured with a driving field of amplitude $H_{ac} = 1$ Oe and frequency $f_{ac} = 10$ Hz. No steady field was applied in the ac susceptibility measurements.

Figure 2(a) shows the resulting dc magnetic susceptibilities χ_{dc}. For most of the Cd–Mg–RE quasicrystals, χ_{dc} is quite large and increases as temperature is decreased. One exception is the Cd–Mg–Yb quasicrystal, where χ_{dc} is roughly 1/1000 of the values for the other Cd–Mg–RE quasicrystals, and is slightly negative for most of the temperatures. With the purity of Yb (99.9 wt.%) in mind, this small χ_{dc} can be attributed to the paramagnetic impurity superimposed on temperature-independent signals from core and itinerant electrons. Hence, Yb is most likely in the non-magnetic divalent state. For the magnetic Cd–Mg–RE quasicrystals, namely RE except for Yb, the inverse susceptibilities χ_{dc}^{-1} are shown in figure 2(b). They are almost linear above 50 K, as expected from the Curie–Weiss law, evidencing the existence of well-localized magnetic moments. Between 50 K and 300 K, the data can be well fitted using the conventional formula,

$$\chi_{dc}(T) = \chi_0 + \frac{N_A \mu_{eff}^2}{3k_B(T-\theta)}, \tag{1}$$

where χ_0, N_A, μ_{eff}, k_B and θ are the temperature independent background, the Avogadro number, the effective moment, the Boltzmann factor and the Weiss temperature, respectively. The estimated μ_{eff} and θ are listed in table 1, together with moments of free RE^{3+} ions calculated from $\mu_{RE^{3+}} = g\sqrt{J(J+1)}\mu_B$, where g is the Landé g-factor and J is the total angular moment. Note that the effective moments μ_{eff} are quite close to $\mu_{RE^{3+}}$. Therefore, it can be concluded that most of the RE atoms are trivalent in the Cd–Mg–RE quasicrystals, and only Yb is divalent. On the other hand, the Weiss temperatures θ are all negative, indicating dominant antiferromagnetic interactions between the RE moments. In figure 3, θ is plotted versus the de Gennes factor $\xi = (g-1)^2 J(J+1)$. As seen in the figure, θ can be well

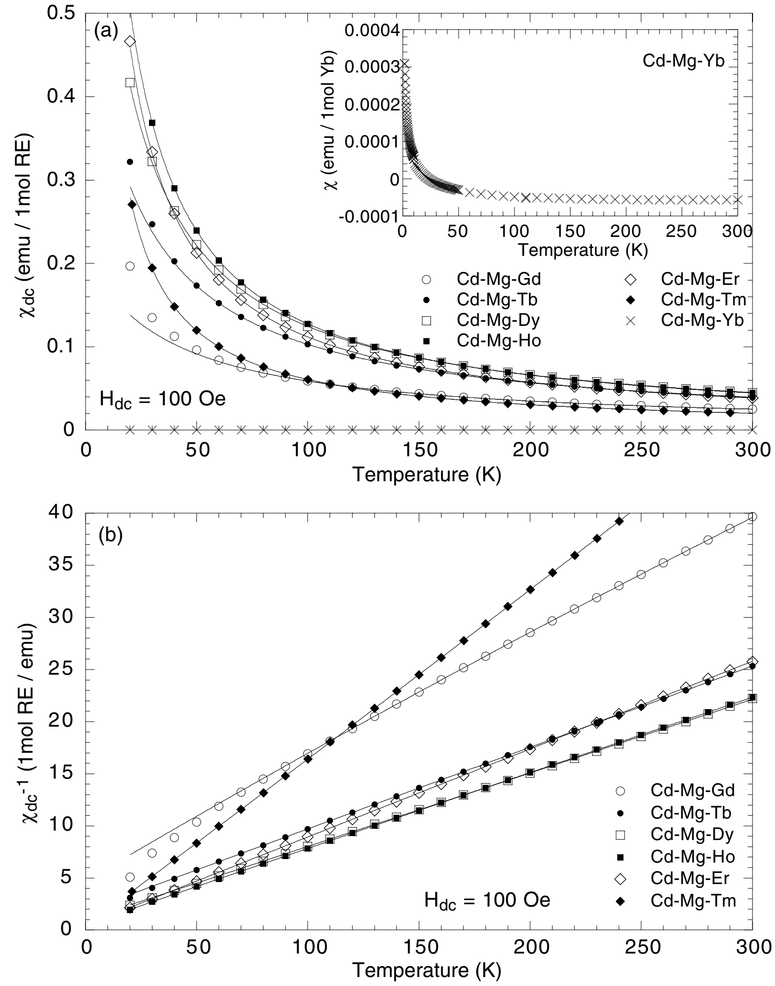

Figure 2. (a) Magnetic susceptibilities of the Cd–Mg–RE quasicrystals measured under H_{dc} = 100 Oe. Inset: magnified plot for the susceptibility of Cd–Mg–Yb. (b) Inverse susceptibilities of the magnetic Cd–Mg–RE quasicrystals. Solid lines show the Curie–Weiss fit.

scaled by ξ. Similar scaling was also reported in the Zn–Mg–RE system [2], and the scaling factors (θ/ξ) for both the systems are almost identical. Since (θ/ξ) is related to electronic structure in the vicinity of the Fermi level [12], this suggests similar electronic structures for the quasicrystals with the trivalent RE atoms, regardless of the difference in the dominant element, i.e. Cd or Zn.

At lower temperatures, the ZFC and FC magnetization were measured under several applied fields to check spin–glass-like freezing, because the freezing was commonly observed in the Zn–Mg–RE quasicrystals. In figure 4(a) the typical result for the Cd–Mg–Tb quasicrystal measured under $H_{dc} = 10$, 300 and 1000 Oe is shown. A difference appears between the ZFC and FC magnetization below $T_{f1} \sim 12.5$ K under $H_{dc} = 10$ Oe, which is the sign of the spin–glass-like freezing [8]. At the higher magnetic fields, the peak at T_{f1} significantly broadens, as usually observed in spin–glasses. As temperature is further decreased, the Cd–Mg–Tb quasicrystal exhibits another anomaly: below $T_{f2} \sim 5.6$ K, the FC magnetization becomes

Table 1. List of the effective moments $\mu_{\rm eff}$ and the Weiss temperatures θ obtained from the Curie–Weiss fit, together with the calculated moments of the free RE^{3+} ions $\mu_{RE^{3+}}$. The freezing temperatures T_{f1} and T_{f2}, determined from the lowest-field dc magnetization (H_{dc} = 10 Oe), are also listed.

	$\mu_{\rm eff}$ (μ_B)	$\mu_{RE^{3+}}$ (μ_B)	θ (K)	T_{f1} (K)	T_{f2} (K)
Cd–Mg–Gd	7.90	7.94	−37	13.0	4.8
Cd–Mg–Tb	10.03	9.72	−23	12.5	5.6
Cd–Mg–Dy	10.67	10.63	−14	7.4	3.8
Cd–Mg–Ho	10.42	10.60	−7	12.5	5.0
Cd–Mg–Er	9.71	9.59	−6	4.4	–
Cd–Mg–Tm	7.08	7.57	−2	–	–

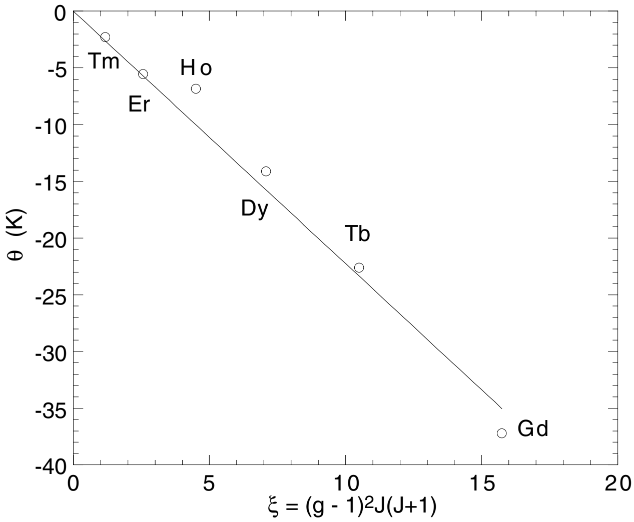

Figure 3. The Weiss temperature θ versus the de Gennes factor $\xi = (g-1)^2 J(J+1)$ for the magnetic Cd–Mg–RE quasicrystals.

rather flat, while the ZFC magnetization begins to decrease more rapidly. The second anomaly can be very clearly seen as a peak in the real part of the ac susceptibility χ'_{ac}, shown in figure 4(b). This suggests further freezing of spins that remain unfrozen at T_{f1}. Similar behaviour was observed for most of the magnetic Cd–Mg–RE quasicrystals: two anomalies were observed for RE = Gd, Tb, Dy and Ho, whereas only one or no anomaly could be detected for RE = Eu or Tm, respectively. The obtained T_{f1} and T_{f2} are summarized in table 1. In view of the small T_{f1} or θ for RE = Er and Tm, we suspect that the second anomaly or both the anomalies will probably be out of the experimental temperature range. Therefore, it is strongly suggested that the two-step freezing, or a set of the two anomalies, is a common characteristic of the Cd–Mg–RE quasicrystals.

The two-step freezing is unlike the freezing observed in the Zn–Mg–RE system or in the canonical spin–glasses. It infers two kinds of relaxation processes that have different characteristic relaxation times τ or, in other words, two peaks in the distribution function of the relaxation time $g(\ln\tau)$. Such double-peaked $g(\ln\tau)$ is suggested for the cluster glass $Fe_{1/4}TiS_2$, and is related to a formation of two types of magnetic clusters [13]. Indeed, a rather

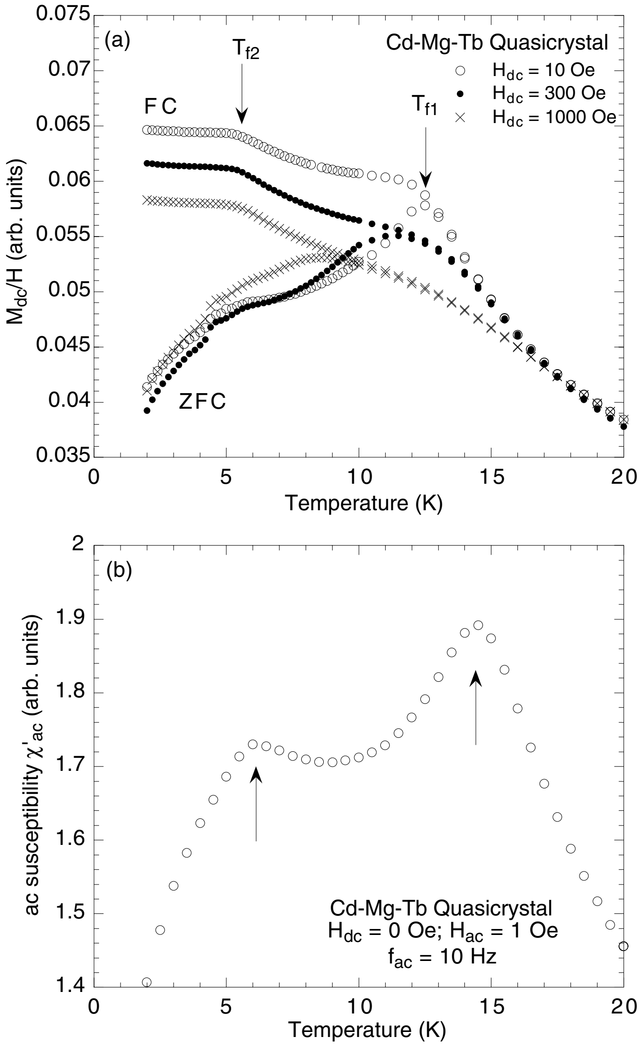

Figure 4. (a) Magnetization curves of the Cd–Mg–Tb quasicrystal measured under $H_{dc} = 10$, 300 and 1000 Oe for the field-cooled (FC) and zero-field-cooled (ZFC) histories. (b) The real part of the ac susceptibility of the Cd–Mg–Tb quasicrystal measured under $H_{ac} = 1$ Oe, $H_{dc} = 0$ Oe and $f_{ac} = 10$ Hz.

favourable situation for the cluster formation may be realized in the Cd–Mg–RE quasicrystals as described below. By comparing the parameters in table 1 to those of the corresponding Zn–Mg–RE quasicrystals, one may find that the freezing temperatures are considerably higher in the Cd–Mg–RE quasicrystals dispite almost identical Weiss temperatures. This presumably indicates that the total strengths of the magnetic interactions are similar in both the systems and that the local competition, or frustration, of magnetic interactions is less dominant in the Cd–Mg–RE quasicrystals. Thus, the neighbouring spins may couple rather easily to form magnetic clusters. However, it is not clear why those magnetic clusters are classifed into two types with different relaxation times, and hence further detailed study, including the frequency dependence of χ_{ac}, is apparently necessary.

A note is necessary on the anomaly at T_{f2}: we simply regard it as freezing in the above. However, there may be a possibility to regard it as antiferromagnetic ordering in view of almost H-independent T_{f2} (figure 4(a)). We, for the present moment, discount this possibility for the following reasons: (1) the successive anomalies bear resemblance to those in the cluster glass $Fe_{1/4}TiS_2$, where two anomalies are clearly attributed to freezing of two different types of magnetic clusters; (2) it may be physically unlikely to order at T_{f2} after partial freezing at T_{f1}. Further study may also be necessary to confirm this point.

Finally, we discuss the stabilization mechanism of the Cd–Mg–RE quasicrystals. To date, it is empirically believed that quasicrystals are stabilized electronically, based on the fact that most of the known quasicrystals are found in a certain range of electron-per-atom ratio e/a. However, as shown above, the Cd–Mg–RE quasicrystals can be formed for both the trivalent and divalent RE atoms, where the e/a ratio obviously differs. Since no significant structural difference was detected in the x-ray or electron diffraction study for the two valences [10], our result casts a serious doubt on the electronic stabilization mechanism for the Cd–Mg–RE quasicrystals.

In summary, the dc and ac magnetization measurements have been carried out for the Cd–Mg–RE quasicrystals. At higher temperatures, the dc magnetization is well represented by the Curie–Weiss law. The estimated effective moments indicate that the RE atoms are mostly trivalent, with the divalent exception Yb. At the lower temperatures, both the dc and ac magnetization show the spin–glass-like freezing. However, the freezing behaviour somehow differs from those observed in the Zn–Mg–RE quasicrystals or in the canonical spin–glasses; it proceeds rather unconventionally in the two successive steps for the Cd–Mg–RE quasicrystals.

Acknowledgments

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