Magnetic properties of the Ag–In–rare-earth 1/1 approximants

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Received 6 October 2010, in final form 1 December 2010
Published 13 January 2011
Online at stacks.iop.org/JPhysCM/23/056001

Abstract

We have performed magnetic susceptibility and neutron scattering measurements on polycrystalline Ag–In–RE (RE, rare-earth) 1/1 approximants. In the magnetic susceptibility measurements, for most of the RE elements, inverse susceptibility shows linear behaviour in a wide temperature range, confirming well localized isotropic moments for the RE$^{3+}$ ions. Exceptionally for the light RE elements, such as Ce and Pr, nonlinear behaviour was observed, possibly due to significant crystalline field splitting or valence fluctuation. For RE = Tb, the susceptibility measurement clearly shows a bifurcation of the field-cooled and zero-field-cooled susceptibility at $T_f = 3.7$ K, suggesting a spin-glass-like freezing. On the other hand, neutron scattering measurements detect significant development of short-range antiferromagnetic spin correlations in the elastic channel, which is accompanied by a broad peak at $\hbar\omega = 4$ meV in the inelastic scattering spectrum. These features have striking similarity to those in the Zn–Mg–Tb quasicrystals, suggesting that the short-range spin freezing behaviour is due to local high-symmetry clusters commonly seen in both systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The static and dynamic behaviour of spins in quasiperiodic structures has been of considerable interest since the early days of quasicrystal research [1]. Theoretically, several quasiperiodic lattices with localized moments have been studied in detail, and a number of intriguing magnetic orderings, including long-range quasiperiodic order, have been proposed to date [2, 3]. Experimentally, however, model materials which contain localized magnetic moments are quite limited even today, and thus the nature of real magnetic quasicrystals remains largely unaddressed. One of the rare examples of magnetic quasicrystals is the Zn–Mg–RE (RE, rare-earth element) icosahedral quasicrystal [4, 5]. For this material, the existence of localized RE$^{3+}$ ions was confirmed by measurements of magnetic susceptibility, which follows the Curie–Weiss law in a wide temperature range [6, 7]. Below a certain low temperature, $T_i = 5.8$ K, a bifurcation of field-cooled (FC) and zero-field-cooled (ZFC) susceptibility is clearly seen. At first sight, it seems that spins in the Zn–Mg–RE quasicrystal freeze randomly, as in canonical spin glasses. However, neutron scattering results revealed that short-range spin correlations develop with collective localized excitations as the temperature decreases [8], which is in striking contrast to the absence of spin correlations in canonical spin glasses [9]. From these observations, it is now established that, on cooling, antiferromagnetic spin correlations first develop in high-symmetry dodecahedral clusters of RE ions, which are essentially present in Zn–Mg–RE icosahedral quasicrystals. Spins in each cluster fluctuate coherently with no inter-cluster correlation. On further cooling to the temperature $T_c$, cluster spin fluctuations freeze in a cluster-spin-glass state without inter-cluster long-range magnetic ordering.

Then, a natural question arises. Why does long-range magnetic order not occur at the low temperature and why are magnetic correlations limited to short-range order? There might be two reasons for this. One is that the quasiperiodicity of the quasicrystal limits the spatial extension of spin correlations. The other is that the spin correlations only develop in the intrinsic high-symmetry RE$^{3+}$ spin clusters, and correlations between the clusters are interrupted with chemical...
or structural disorder which commonly exists in quasicrystals and approximants.

In order to come to a conclusion about this issue, it is worth studying the magnetic ordering behaviour and spin correlations in magnetic approximants, which have a periodic lattice and include periodically arranged magnetic clusters which consist of localized spins, unlike quasicrystals.

After the discovery by Guo and Tsai [10] of an icosahedral quasicrystal in Ag$_{42}$In$_{42}$Yb$_{16}$, formation of the 1/1 approximants was identified in most Ag–In–RE alloys [11, 12]. These 1/1 approximants are considered as isostructural to the well-known Cd$_6$Yb approximant [13–16], which is a bcc crystal of the space group $Im\bar{3}$ with icosahedral clusters of RE elements and forms the same local structure as the stable binary icosahedral quasicrystal Cd$_5$Yb$_{17–19}$. This was the first approximant phase to be discovered which contains magnetic REs and does not contain neutron-absorbing elements such as Cd. Therefore these approximants enable us to perform a microscopic neutron-scattering investigation of the magnetic properties of high-symmetry magnetic clusters arranged periodically. Although the local atomic structure is different from that in the Zn–Mg–RE quasicrystals [20, 21], in which the symmetry of the RE clusters would be dodecahedral, study of the magnetic properties of the Ag–In–RE approximant will provide a key to solving our question in view of the high symmetry of the icosahedral magnetic clusters. In this work, we have performed magnetic susceptibility and neutron scattering measurements on polycrystalline Ag–In–RE 1/1 approximants. The magnetic susceptibility versus temperature for 12 Ag–In–REs (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) showed no anomaly due to long-range magnetic order. For most of the samples, the inverse susceptibility follows linear behaviour above 100 K, which suggests that the RE ions in these samples are isotropically well localized. At low temperature near 3 K, a spin-glass-like bifurcation of the FC and ZFC magnetic susceptibility was observed for RE = Eu, Gd, Tb and Dy. In the neutron elastic and inelastic scattering measurements, which were performed for RE = Tb, development of diffuse scattering was observed as temperature decreases in addition to a broad peak at $\hbar\omega = 4$ meV. These results indicate that the spin fluctuations freeze into a cluster-spin-glass with short-range magnetic order, which shows very good correspondence to those in the Zn–Mg–Tb quasicrystal.

2. Experimental details

For magnetic susceptibility measurements, polycrystalline samples of the Ag–In–RE (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) 1/1 approximants were prepared by means of melting constituent elements in an arc furnace. The purity of the starting elements was 99.9999% for Ag, 99.9999% for In and 99.9% for the RE. Most of the nominal compositions for the polycrystal preparation were decided by an earlier report [12] and are shown in figure 1. The resulting
as-cast alloys were wrapped in Mo foils, sealed in quartz tubes under a pure Ar atmosphere and subsequently heat-treated at 823 K for 100 h. For the neutron scattering experiments, a different procedure was chosen to prepare as much as 10 g of an alloy; a polycrystalline sample of Ag$_{49}$In$_{37}$Tb$_{14}$ was synthesized directly from the constituent elements in an Al$_2$O$_3$ crucible, sealed in a quartz tube, heat-treated at 1273 K in an electric furnace. The elements were put into a high-purity Al$_2$O$_3$ crucible, sealed in a quartz tube, heat-treated at 1273 K for 10 h and heat-treated again at 923 K for 100 h.

The phase quality of the resulting samples was characterized by x-ray powder diffraction (Rigaku, Miniflex) and scanning electron microscopy (SEM) (JEOL, JSM-5600). In addition, their compositions were determined by energy dispersive x-ray spectroscopy (Oxford Instruments, Link ISIS). In addition, their compositions were determined by energy dispersive x-ray spectroscopy (Oxford Instruments, Link ISIS). Magnetic susceptibility was measured between 2 and 300 K by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL) with an external dc field of 100 Oe. Neutron elastic, quasielastic and inelastic scattering experiments were carried out on the polycrystalline Ag$_{49}$In$_{37}$Tb$_{14}$ sample. For thermal-neutron experiments, we used the triple-axis spectrometer ISSP-GPTAS installed at the JRR-3 research reactor (Tokai, Japan). To minimize the neutron absorption effect of In atoms, the powdered sample was inserted into a double-cylindrical annular Al cell with a sample thickness of $t = 1.5$ mm. For the elastic scattering experiment, the spectrometer was operated in double-axis mode with an incident energy of $E_i = 13.7$ meV and with collimations of $40'–80'–40'$. To eliminate higher harmonic neutrons, two pyrolytic-graphite (PG) filters were inserted between the source and the monochromator, and between the sample and the analyser. For the thermal-neutron inelastic scattering experiment, the triple-axis mode was employed with a doubly (horizontally and vertically) focusing analyser selecting the final neutrons with $E_f = 14.7$ meV. The incident side collimations were $40'–40'$, whereas a radial collimator (Rad) and a slit of 30 mm width were inserted into the outgoing path. The energy resolution was 1.3 meV in full-width at half-maximum (FWHM) at the elastic position. Furthermore, for quasielastic scattering experiments in higher energy resolution, the cold-neutron triple-axis spectrometer ISSP-HER installed at the C1 guide tube of JRR-3 was used. A doubly focusing analyser was employed to fix the final energy to $E_f = 3.0$ meV with the collimations Guide-Open-Rad-Slit (20 mm), yielding an energy resolution of 0.1 meV (FWHM) at the elastic position. Finally, powder neutron inelastic scattering experiments on Zn–Mg–Tb magnetic quasicrystals were performed as in the supplement of [8], using the inverted-geometry time-of-flight spectrometer LAM-40 [22] at KENS, KEK, Japan. PG 002 reflections were used for the analyser to fix the final energy at $E_f = 4.9$ meV, and the energy resolution was estimated using a vanadium standard as 0.32 meV (FWHM) at the elastic position.

### 3. Sample characterization

Figure 1(a) shows the x-ray powder diffraction patterns of the prepared polycrystalline samples. As seen in the figure, formation of the 1/1 approximant phase was confirmed as the major phase for all the RE elements. On the other hand, small impurity peaks were also found for RE = Gd, Tb, Ho, Er and Tm, which indicate the existence of a small amount of contaminating phases. Representative examples of SEM micrographs for RE = Tm and Gd are shown in figures 1(b) and (c). In each micrograph, we observed two phases with different compositions; composition of the major phase was roughly equal to the nominal one, which also suggests that the main phase was 1/1 approximant. The other minority phase was Ag$_3$In or Ag$_{10}$In$_{65}$RE$_{25}$. Such contamination was more or less observed in every RE sample, including the Ag–In–Tb sample for neutron experiments. Each impurity phase was, however, tiny in volume; thus the deviation of the nominal composition from the ideal one of the 1/1 approximant phase was sufficiently small. From these results, we can conclude that 1/1 approximants were formed as the major phase in all the Ag–In–RE samples.

### 4. Magnetic susceptibility

The temperature dependence of magnetic susceptibility for all the prepared polycrystalline samples is shown in figure 2(a). No clear anomaly due to long-range magnetic order could be observed for any of the RE samples. We note that a weak anomaly for RE = Eu is due to ferromagnetic transition of the Eu$_2$O$_3$ impurity phase, which inevitably appears in the

**Figure 2.** (a) Temperature dependence of magnetic susceptibility for all the RE samples prepared in the present work observed under an external field $H_{ext} = 100$ Oe. Inset: field-cooled and zero-field-cooled susceptibility for RE = Tb in the low temperature region. (b) Inverse susceptibility for all the RE samples.
polycrystalline grains because of the highly oxidizing nature of Eu. For \( \text{RE} = \text{Sm} \) and \( \text{Yb} \), the magnetic susceptibility is very small, showing only an impurity upturn at low temperatures. This suggests that these RE ions are in the non-magnetic divalent state. Inverse susceptibility is also shown in figure 2(b). The inverse susceptibility for \( \text{RE} = \text{Ce} \) and \( \text{Pr} \) is not linear, even at room temperature, indicating that there is considerable crystal-field-splitting corresponding to the energy scale of 300 K or a valence fluctuation effect [23]. In the other RE samples (\( \text{RE} = \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er} \) and \( \text{Tm} \)), the inverse susceptibility shows linear behaviour above 100 K. An effective moment size \( \mu_{\text{eff}} \) and a Weiss temperature \( \theta \) were obtained by fitting the inverse susceptibility to the Curie–Weiss law:

\[
\frac{1}{\chi} = \frac{N\mu_{\text{eff}}^2\mu_B^2}{3k_B(T-\theta)} + \chi_0
\]

where \( k_B \), \( N \), \( \mu_B \) and \( \chi_0 \) are the Boltzmann factor, the number of magnetic ions in unit volume, the Bohr magneton and temperature independent susceptibility, respectively. \( \mu_{\text{eff}} \) and \( \theta \) are given in table 1 together with calculated magnetic moment sizes for free \( \text{RE}^{3+} \) (and \( \text{RE}^{2+} \) for \( \text{RE} = \text{Eu} \)) ions. As can be seen in the table, observed effective moments are in good agreement with theoretical free ion values for \( \text{RE}^{3+} \) (or \( \text{RE}^{2+} \) for \( \text{RE} = \text{Eu} \)), confirming the well localized isotropic nature of the magnetic moments. Except for \( \text{RE} = \text{Eu}, \theta \) is negative, indicating dominant antiferromagnetic interactions between magnetic moments. It is noteworthy that \( \theta \) decreases as the RE becomes heavier from Gd to Tm, namely \( \theta \) is well scaled by the de Gennes factor, suggesting that electronic states are equal at the Fermi level for different RE samples (cf [6]).

At the low temperature of \( \sim 3 \) K, a spin-glass-like bifurcation of the FC and ZFC magnetic susceptibility was observed for \( \text{RE} = \text{Eu}, \text{Gd}, \text{Tb} \) and \( \text{Dy} \). Representative susceptibility at low temperature for \( \text{RE} = \text{Tb} \) is shown in the inset of figure 2(a). A clear bifurcation is seen at and below the freezing temperature \( T_f = 3.7 \) K, suggesting a spin-glass-like freezing. The temperature \( T_f \) is also listed in table 1. We note that for \( \text{RE} = \text{Tb} \), \( T_f \) is the highest among those which show freezing behaviour. A ratio \( |\theta/T_f| \) is approximately 10 for \( \text{RE} = \text{Tb} \), and thus this is classified as a highly frustrated magnet.

### Table 1. Observed Weiss temperatures \( \theta \), effective moment sizes \( \mu_{\text{eff}} \), freezing temperatures \( T_f \) and calculated moment sizes for free \( \text{RE}^{3+} \) (and for \( \text{RE}^{2+} \) for \( \text{RE} = \text{Eu} \)).

| RE   | \( \mu_{\text{eff}} \) | \( \mu_{\text{RE}^{3+}} \rangle \text{ calc.} \) | \( \theta \) (K) | \( T_f \) (K) |
|------|------------------------|---------------------------------|----------------|--------------|
| Nd   | 4.543(4)               | 3.6                             | -23.23(18) | —            |
| Eu   | 8.2(8)                 | 0.0 (7.94)                       | 6(16)        | 2.5          |
| Gd   | 8.895(3)               | 7.94                            | -55.5(9)    | 3.3          |
| Tb   | 10.77(7)               | 9.72                            | -34.13(14)  | 3.7          |
| Dy   | 11.262(10)             | 10.6                            | -17.69(18)  | 2.5          |
| Ho   | 11.638(7)              | 10.6                            | -12.09(12)  | —            |
| Er   | 9.74(6)                | 9.59                            | -5.58(18)   | —            |
| Tm   | 8.490(4)               | 7.57                            | -3.96(6)    | —            |

* For \( \text{RE}^{2+} \).

Figure 3. (a) Neutron powder diffraction patterns at \( T = 60 \) K (open triangles) and 3 K (open squares) in the Ag–In–Tb 1/1 approximant observed in double-axis mode. Vertical solid lines at the bottom represent nuclear Bragg positions for the 1/1 approximant phase. (b) The open circles represent the difference between \( T = 3 \) and 60 K patterns (\( I(3 \text{K}) - I(60 \text{K}) \)). The solid line is a guide to the eye.

5. Neutron scattering

To investigate the spin freezing behaviour at low temperature microscopically, we have performed neutron elastic and inelastic scattering experiments. For these neutron experiments, we selected the \( \text{RE} = \text{Tb} \) sample because it has the highest freezing temperature. This means that energy scale is the highest among Ag–In–RE 1/1 approximants and makes an inelastic experiment feasible.

Neutron powder diffraction patterns observed at the lowest temperature \( T = 3 \) K and paramagnetic temperature \( T = 60 \) K are shown in figure 3(a). At 60 K, all the Bragg peaks were indexed by nuclear reflections of the 1/1 approximant phase, as shown by vertical solid lines in the bottom part of the figure. It follows that the impurity phase in the sample used in the neutron experiment is too small to be obviously detected. On cooling to 3 K, no additional Bragg reflection appears in the diffractogram. This confirms the absence of long-range magnetic order in the Ag–In–Tb 1/1 approximant. On the other hand, there is a weak but definitely observable increase in magnetic diffuse scattering intensity at the lowest temperature. To visualize this increase more clearly, the temperature difference between the two diffraction patterns,
Temperature dependence of diffuse scattering intensity at 2θ = 20.3° of Zn–Mg–Tb quasicrystal measured at LAM-40 with an energy resolution of ΔE = 0.32 meV. The solid lines are guides to the eye. (b) Temperature dependence of quasielastic spectra between 250 and 0.7 K. (c) Some fitting results of the quasielastic spectra showing contributions of total, elastic, quasielastic and constant background resolution of Δ1. (d) Temperature dependence of quasielastic peak width Γ (half-width at half-maximum) obtained by fitting the spectra of (b) to a model scattering function (2).

Figure 4. (a) Temperature dependence of diffuse scattering intensity observed with higher energy resolution ΔE = 0.1 meV. Inset: Temperature dependence of diffuse scattering intensity at 2θ = 20.3° of Zn–Mg–Tb quasicrystal measured at LAM-40 with an energy resolution of ΔE = 0.32 meV. The solid lines are guides to the eye. (b) Temperature dependence of quasielastic spectra between 250 and 0.7 K. (c) Some fitting results of the quasielastic spectra showing contributions of total, elastic, quasielastic and constant background resolution of Δ1. (d) Temperature dependence of quasielastic peak width Γ (half-width at half-maximum) obtained by fitting the spectra of (b) to a model scattering function (2).

or I (3 K)–I (60 K), is shown in figure 3(b). Broad peaks are apparently seen at Q = 0.85 and 1.8 Å⁻¹. The appearance of diffuse scattering peaks suggests the development of magnetic short-range order at the base temperature. The temperature difference becomes negative at Q → 0, indicating that dominant spin correlations are antiferromagnetic, which is consistent with the negative Weiss temperature θ. From the width of the first diffuse scattering peak at Q = 0.85 Å⁻¹, we estimate the correlation length as ξ ∼ 9 Å (FWHM). It is noted that the diameter of a single icosahedral cluster of Tb ions in the Ag–In–Tb 1/1 approximant phase is approximately 11 Å, and thus the observed spin correlation length corresponds to the diameter.

Next, evolution of the short-range spin correlations was investigated by observing the temperature dependence of the diffuse scattering peak at Q = 0.85 Å⁻¹. Since the peak was considerably broader in the Q space, we utilized a horizontally focusing analyser in triple-axis mode to gain higher counting statistics in limited beam time, collecting scattering intensity in a Q-range of 0.74 Å⁻¹ < Q < 0.96 Å⁻¹. An observed spectrum is shown in figure 4(a). It can be seen in the figure that the intensity of the diffuse scattering increases gradually below T = Tdiffuse = 60 K. Tdiffuse was determined by using a cross-over between the two linear regimes. Hence, we can conclude that short-range spin correlations develop at the temperature Tdiffuse, which is significantly larger than the freezing temperature Tf = 3.7 K. In principle, Tf and Tdiffuse can be different, because magnetometry and neutron scattering measurements detect fluctuations of different time scales (the order of a few seconds for the former, but around 10⁻¹² s for the latter). The ratio of the two temperature scales, Tf/Tdiffuse ≃ 0.06, is surprisingly smaller than those of canonical spin glasses [24].

To elucidate this slowing-down process of spin fluctuations, the neutron quasielastic signal was investigated. Several inelastic scattering spectra observed at Q = 0.85 Å⁻¹ with T = 0.75, 3.5, 10, 20, 30, 45, 60, 100, 150, 200 and 250 K are shown in figure 4(b). Quasielastic tails were observed at high energy transfers, suggesting that the spectra were then fitted, convoluted with the instrumental resolution, to the following scattering function including a Lorentzian spectral weight function with the width Γ:

$$S(\hbar\omega; T) = C_{\text{elastic}}\delta(\hbar\omega) + C_{\text{qel}}$$

$$\times \frac{1}{1 - \exp(-\hbar\omega/k_BT)} \frac{\Gamma_{\hbar\omega}}{(\hbar\omega)^2 + \Gamma^2} + C_{\text{bg}},$$

(2)
where the first, second and third terms represent elastic, quasielastic and constant background functions. In the fitting procedure, \( C_{\text{elastic}} \) was fixed to a value determined by the spectrum at \( T = 250 \) K. Some fitting results showing each contribution are shown in figure 4(c). Solid, dash-dotted, dashed and dotted lines represent total, elastic, quasielastic and background functions, respectively. Temperature dependence of the obtained half-width at half-maximum \( \Gamma \) is shown in figure 4(d). In a higher temperature range \( 100 \) K < \( T \) < 250 K, \( \Gamma \) shifted moderately. In contrast, the width suddenly decreased below 100 K. This indicates that the spins drastically slow down in this temperature range. This is consistent with the increase in the elastic signal below \( T_{\text{diffuse}} \approx 60 \) K shown in figure 4(a). Since the quasielastic width eventually becomes almost zero at temperatures close to \( T_{f} \), it is pointed out that the corresponding relaxation is indeed responsible for the freezing behaviour observed in the macroscopic measurements.

To obtain further insight into faster spin dynamics, we performed inelastic neutron scattering experiments in a wider energy range up to 10 meV. The experiment was carried out using the energy resolution of \( \Delta E = 1.3 \) meV. The resulting temperature variation of the inelastic spectrum is shown in figure 5(a). At high temperature, such as \( T = 150 \) K, the inelastic spectrum was again dominated by a broad quasielastic signal centred at \( \hbar \omega = 0 \). As the temperature decreases, an inelastic scattering peak emerged below 60 K with the peak energy shifting to 4 meV toward the base temperature. In view of this considerably broader energy width at high temperature, the origin of the quasielastic signal should be interpreted as different from that of the narrow quasielastic peak observed with the higher energy resolution experiment shown in figure 4(b). In addition to the measurement, \( Q \) dependence of the inelastic peak at \( \hbar \omega = 3.9 \) meV is shown in figure 5(b). \( Q \) dependence of intensity corresponds to the square of the magnetic form factor of the Tb\(^{3+} \) ion [25], confirming the magnetic origin of the inelastic peak.

Apparent crystalline field splitting is ruled out as the possible origin of the peak in view of the temperature dependence of the peak and good linearity of the inverse magnetic susceptibility even at low temperature for \( \text{RE} = \text{Tb} \). It is emphasized that the temperature at which the inelastic peak emerges roughly corresponds to \( T_{\text{diffuse}} \), suggesting a close relation between formation of the short-range correlations and the inelastic peak.

### 6. Discussion

In the present study, we found that some of Ag–In–RE 1/1 approximants exhibit macroscopic spin freezing behaviour in magnetic susceptibility measurements, similar to the behaviour of canonical spin glasses. On the other hand, three distinct features from canonical spin glasses have been revealed in the neutron scattering results for the \( \text{RE} = \text{Tb} \) sample. First, significant short-range spin correlations appear at the lowest temperature, in contrast to completely random freezing in canonical spin glasses. Second, development of the diffuse scattering starts at fairly higher temperature \( T_{\text{diffuse}} \approx 60 \) K compared with the macroscopic freezing temperature \( T_{f} \approx 3.7 \) K. Third, another considerably broader quasielastic component appears at high temperature \( T > T_{\text{diffuse}} \) and changes into a broad inelastic peak at \( \hbar \omega = 4 \) meV as the short-range correlation is formed.

These totally unique results suggest the following two-step freezing process in the 1/1 approximant: first of all, at \( T > T_{\text{diffuse}} \), individual spin fluctuations have no spatial correlation, giving rise to the considerably broader quasielastic signal. As the first step of freezing, below \( T_{\text{diffuse}} \), spatial correlation of spin fluctuations starts to develop. Spins in each magnetic cluster fluctuate coherently, or intra-cluster spin correlations develop, because the length scale of the short-range spin correlation corresponds to that of the icosahedral spin cluster of Tb ions, which is a characteristic magnetic block.
in the 1/1 approximant phase. Moreover, the clusters formed by correlated spins probably have collective excitation modes and lead to the inelastic peak at 4 meV. An enhancement of the intra-cluster spin coherence with cooling would lead the inelastic intensity to increase and increase the energy up to 4 meV from 0 meV. As the second step, with further cooling, fluctuations of the spin clusters become slower and slower, as shown by the width $\Gamma$ in the narrower quasielastic spectrum, and eventually cluster fluctuations freeze at $T_i$ of the order of seconds. Thus we have cleared up the difference in the freezing behaviour in the Ag–In–Tb 1/1 approximant and that seen in the canonical spin glasses.

In this paragraph, in contrast, we point out the great similarities between the present approximant and the Zn–Mg–Tb magnetic quasicrystal. The first similarity in both systems is the well localized isotropic Tb$^{3+}$ ions and the random spin-glass-like freezing, indicated by Curie–Weiss behaviour in a wide temperature range and apparent bifurcations at low temperature in macroscopic susceptibility measurements. Variations of characteristic parameters are described below; freezing temperature $T_i$ and a Weiss temperature $\theta$ are 3.7 and $-34$ K for the Ag–In–Tb 1/1 approximant of the present study, whereas they are 5.8 and $-26.3$ K for the Zn–Mg–Tb quasicrystal [7]. A frustration parameter $|\theta/T_i|$ is about two times larger in the 1/1 approximant than the quasicrystal. Thus the approximant would have a higher degree of frustration. This may be due to the weaker intrinsic structural disorder expected for the crystalline approximant phase. The next similarity is the existence of short-range spin correlation. In particular, the correlation length is of the same degree as the diameter of the magnetic atom cluster in each sample. The correlation length at the base temperature is about 20 Å (FWHM) for the quasicrystal and 9 Å (FWHM) for the approximant. The diameter of the magnetic clusters are 15 Å [21] and 11 Å, respectively. These relations lead to the idea that clusters commonly form rigid spin objects approximately by the cluster at low temperature. Furthermore, the temperature scale at which the short-range-correlated spin fluctuations fall into the elastic time window of the neutron experiment is mostly the same; the diffuse scattering intensity increases around 60 K in both systems as shown by figure 4(a). Therefore, the temperature scales of the diffuse scattering are not scaled by the freezing temperature $T_i$ but rather by the Weiss temperatures $\theta$, which is mostly the same in both systems. This is quite reasonable, since it is the Weiss temperature which provides a rough estimate of the strength of the inter-spin interactions. It is further suggested that the inter-spin interactions are of a similar strength in both systems. The third point is the broad inelastic peak at low temperature, which is at 4 meV in the approximant and 2 meV in the quasicrystal. The energy difference possibly reflects the variation of the cluster.

As seen above, the magnetic freezing behaviour of formation of short-range spin correlations around 60 K and its freezing at the low temperature $T_i$ is quite in common in the two seemingly different samples, i.e. the approximant with periodically arranged magnetic clusters and the quasicrystal with quasiperiodically arranged magnetic clusters. This indicates evidently that a key to explaining the freezing behaviour without long-range magnetic order in the two systems is the local highly symmetric cluster; a dodecahedral cluster for the Zn–Mg–Tb quasicrystal and an icosahedral one for the Ag–In–Tb 1/1 approximant. Thus, we would suggest that long-range quasiperiodicity is not the origin of the freezing behaviour in the magnetic quasicrystal.

7. Summary

We have performed combined magnetic susceptibility and neutron scattering measurements on the Ag–In–RE 1/1 approximants. In the magnetic susceptibility measurements, it has been shown that for most of the RE elements, Ag–In–RE approximants have well localized isotropic moments. Exceptionally for RE = Ce and Pr, crystalline field splitting or valence fluctuation effects would hinder linear Curie–Weiss behaviour. For $RE = Sm$ and Yb, they are in non-magnetic divalent states. Especially for $RE = Eu$, Gd, Tb and Dy, which contains isotropic localized moments, a bifurcation of the FC and ZFC magnetic susceptibility was observed at the low temperature of 3 K, suggesting a spin-glass-like freezing of the spins. In the neutron scattering measurements for $RE = Tb$, significant diffuse scattering below $T_{\text{diffuse}} = 60$ K was detected, which was accompanied by the evolution of the broad inelastic peak at $h\omega = 4$ meV. From these measurements, a two-step freezing behaviour was revealed. Below 60 K, intra-cluster antiferromagnetic spin correlations in icosahedral clusters start to develop. Upon further cooling to low temperature $T_i = 3.7$ K, the cluster spin fluctuations freeze without inter-cluster long-range magnetic ordering. The freezing process is semi-quantitatively identical to that observed in the Zn–Mg–Tb quasicrystal, indicating that the origin of the spin freezing behaviour is not quasiperiodicity but the high symmetry of their magnetic cluster.

Acknowledgments

The authors thank Drs A P Tsai and H Takakura for valuable comments and stimulating discussions. This work is partly supported by the Grand-in-Aid for the basic research (C) from MEXT, Japan.

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