Memory and rejuvenation in a quasicrystal

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Abstract – The glassy features of a single crystal of the icosahedral quasicrystal \(i\)-GdCd\(_{7.5}\) were investigated by means of squid magnetometry. The temperature-dependent zero-field–cooled magnetization was recorded on re-heating from low temperatures after halts in the cooling. The results evidence dynamical features akin to those of archetypal spin glasses, such as aging, memory, and rejuvenation. The results are compared to those of model spin glasses with different spin dimensionality, suggesting a qualitative similarity to the behaviour of metallic RKKY “Heisenberg” spin glasses.

Introduction. – Quasicrystals (QCs) are a group of materials, mostly of intermetallic components, with long-ranged aperiodic atomic structures displaying symmetries incompatible with three-dimensional periodicity [1–3], whose details and properties are still to be understood [4,5]. Interestingly, magnetic rare-earth elements may be included in the quasicrystals, yielding magnetic interaction [6]. In order to extract information of the mechanisms determining the magnetic interactions in QCs, it is common to investigate the so-called approximants of quasicrystals (ACs) which are periodic crystals with similar local structure as the QCs [7]. Long-ranged ferromagnetic, antiferromagnetic and ferrimagnetic order has been reported in ACs [8–10]. Although there is no report of long-range magnetic order for QCs, spin-glass-like [11,12] properties have been consistently reported [4,6]. It may be reasonable to expect magnetic frustration in such systems, owing to the symmetry, aperiodic structure and potential disorder in magnetic interaction. The magnetic interaction is often assumed to be of Ruderman-Kittel-Kasuya-Yosida (RKKY) type in the QCs and ACs [13,14].

A relatively simple way to evidence glassy dynamics is to perform so-called memory experiments [15] in magnetization measurements. Such experiments have been used to demonstrate the glassy aging and rejuvenation [16] of the spin configuration of model spin glasses [15,16], superspin glasses (collective states of interacting magnetic nanoparticles) [17], geometrically frustrated systems [18], as well as exotic “CE-glasses” [19] and “chiral-glass” superconductors [20]. In the present paper, we describe in detail the protocols and results of memory experiments and employ them on a \(i\)-GdCd\(_{7.5}\) quasicrystal. The observed aging and memory features of the quasicrystal are found to be qualitatively similar to those of model spin glasses, especially from the Heisenberg universality class.

Experimental. – A single crystal of the \(i\)-GdCd\(_{7.5}\) QC was synthesized using the self-flux method. Similar conditions as reported by Goldman et al. [6] were used. In the present synthesis, elemental granules of Gd with purity 99.99 at.% and Cd with purity 99.999 at.% were used. A total mass of 7g with starting nominal composition Gd\(_{0.8}\)Cd\(_{99.2}\) was used. The mixture was first heated to 700°C and slowly cooled to 355°C where the QC grains were separated from the Cd excess flux by centrifuging. The resulting sample was first analyzed by X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX). XRPD patterns further confirms the phase purity of the QC sample (fig. 1(a)). Elemental analysis using the energy dispersive X-ray spectroscopy (EDX) method taken

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Fig. 1: (a) XRPD pattern and (b) optical microscope image for i-GdCd$_{7.5}$ QC. Diffraction background, Bragg-peaks from Cu-K$_{α2}$ have been corrected for clarity. Bragg-peaks from residual Cd are indicated by red asterisks. (c) The icosahedral atomic shells in GdCd$_6$ 1/1 AC, decorated by Gd atoms; a similar shell is expected in the related i-GdCd$_{7.5}$ QC.

Fig. 2: (a) Temperature-dependent magnetization $M(T)$ measured under ZFC and FC conditions with $H = 10$ Oe. (b) The field dependence of the magnetization $M(H)$ recorded at $T = 2$ K. The inset shows the $M(H)$ curve with $M$ represented in $\mu_B$/Gd.

Results and discussion. – The temperature dependence of the zero-field–cooled (ZFC) and field-cooled (FC) magnetization $M$, and ac-susceptibility were recorded using a superconducting quantum interference design (SQUID) from Quantum Design Inc, equipped with the ultralow field option.

Magnetic-field–$H$–dependent magnetization measurements were recorded on the same equipment at low temperatures.

from 20 points on a cross-section polished sample resulted in an average value of GdCd$_{7.5(5)}$; a value in good agreement with the expected value. Figure 1(a), (b) shows a XRPD pattern and an optical microscopy image of the title compound; millimeter-sized pentagonal dodecahedral facets of the QC are clearly visible. Expected diffraction peaks from an i-GdCd$_{7.5}$ QC were identified in the present compound [6]; peaks from residual Cd flux are indicated. Figure 1(c) illustrates the icosahedral shell formed by 12 Gd atoms in the GdCd$_6$ AC. A similar icosahedral shell is envisioned in the related i-GdCd$_{7.5}$ QC; note that only one of the five shells is shown in the figure. The magnetic properties, including the temperature-dependent zero-field–cooled (ZFC) and field-cooled (FC) magnetization $M$, and ac-susceptibility were recorded using a superconducting quantum interference design (SQUID) from Quantum Design Inc, equipped with the ultralow field option.
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Fig. 3: (a) Temperature dependence of inverse magnetic susceptibility after performing the background correction, \((\chi - \chi_0)^{-1}(T)\) recorded at \(H = 5\, \text{kOe}\), where \(\chi_0\) is the background correction term. The solid line is the best fit of \((\chi - \chi_0)^{-1}(T)\) to the Curie-Weiss equation. The temperature variation of \(\chi(T)\) is shown in the inset for reference. (b) Temperature dependence of real and imaginary component of ac-susceptibility \(\chi_{ac}(T)\) recorded at three different frequencies \(f = 1.7, 17\) and \(170\, \text{Hz}\). The zoomed view of in phase component of \(\chi_{ac}\), i.e., \(\chi'\) is shown in the inset; ac-amplitude \(H = 4\, \text{Oe}\).

Fig. 4: Illustration of the memory experiments. (a) Schematic of the memory experiment protocol, illustrating the cooling and reheating of an ordinary ZFC measurement (black curve) and another one including a halt at a constant temperature \(T_{\text{halt}}\) during the initial cooling to the lowest temperature (blue curve). (b) Typical relaxation curves for the ZFC magnetization of a spin glass, recorded in a magnetic field applied immediately \((t_{\text{halt}} = 0)\) and \(t_{\text{halt}} = 3000\, \text{s}\) after reaching \(T_{\text{halt}}\). The dotted line marks the typical observation time in \(M(T)\) measurements, \(\sim 30\, \text{s}\) (c) Typical temperature dependence of the ZFC magnetization curves of a spin glass, recorded on reheating after cooling down to the lowest temperature (reference, black color) and including a halt at \(T_{\text{halt}}\) for 3000 s during the initial cooling. The dotted line marks \(T_{\text{halt}}\). The experimental data used in the sketch can be found in ref. [21].

magnetization curves are similar to those reported earlier [6], with a cusp in the ZFC magnetization just below \(T = 5\, \text{K} (T_f \sim 4.7\, \text{K})\). The FC magnetization is similar to the ZFC one for temperatures above the ZFC cusp. Below the cusp, the FC magnetization curve departs from the ZFC one, only decreasing slightly as the temperature is lowered below \(T = 5\, \text{K}\). The observed behavior is reminiscent to that of spin glasses [12,15].

Figure 2(b) shows the magnetic-field–dependent \(M(H)\) curve recorded at \(T = 2\, \text{K}\). It is seen in the figure that the magnetization only increases slightly and nonlinearly with the applied magnetic field, well below the value \(gJ = 7\, \mu\text{B}/\text{Gd} (J = 7/2; g = 2)\) even in magnetic fields of \(50\, \text{kOe} (M(H = 50\, \text{kOe}) \sim 8.1\, \text{emu/g}, \text{which corresponds to about} 1.45\, \mu\text{B}/\text{Gd})\), in agreement with the spin glass behavior suggested by the \(M(T)\) curves. The ZFC \(M(T)\) magnetization data recorded in \(H = 5\, \text{kOe}\) is shown in the inset of fig. 3(a). The inverse of the corresponding susceptibility data \(M/H\) is plotted in the main frame of the figure. As observed for many QCs and ACs, the inverse susceptibility data closely follows a Curie-Weiss behavior, here for all temperatures above \(T = 5\, \text{K}\). From the linear
fitting of the data, a Curie-Weiss temperature $\theta \sim -37$ K and the effective moment $\mu_{\text{eff}} \sim 8.0 \mu_B$ could be estimated. The $\theta$ and $\mu_{\text{eff}}$ values are very close to the values reported earlier for this system [6] and also for its approximant crystal [9]. The $\mu_{\text{eff}}$ value is nearly that expected from the $g[J(J+1)]^{1/2} \sim 7.94\mu_B$ value, while the negative $\theta$ value suggests a significant antiferromagnetic interaction.

The temperature dependence of the ac-susceptibility $\chi(\omega,T)$ was recorded using an excitation $h = 4$ Oe for different frequencies. A weak frequency dependence of the in-phase component of the susceptibility is observed below the cusp temperature (see fig. 3(b)); however the magnetic signal was too low to be investigated in more detail, and, e.g., evidence critical slowing down and a spin glass phase transition [22]. One can however determine whether the system displays glassy dynamical features at low temperatures. When a spin glass is rapidly cooled down to a glassy phase and kept at a constant temperature, the random spin configuration acquired during cooling will rearrange itself or age (e.g., by droplet excitations [23]). To evidence such aging, the material may be zero-field–cooled down to a low temperature, and its magnetization recorded as a function of time after applying a small, probing [15], magnetic field —yielding ZFC relaxation $M(t)$ curves. As seen in the sketch in fig. 4(b), as a result of the aging phenomenon, the ZFC $M(t)$ curves of a spin glass recorded after a halt time lie significantly below those recorded immediately after reaching the halt temperature and applying the probing dc field. The shape of the curves is also different [16]. The dynamical features of a spin glass may be determined from more easily measured temperature-dependent ZFC magnetization curves, owing to a unique property of spin glasses. The spin glass may indeed at the same time “remember” its aging (memory effect) and “forget” it (rejuvenation effect), if it is subjected to temperature changes subsequent to the halt [15,24]. Such memory experiments are illustrated in fig. 4(c), which shows the typical temperature dependence of the ZFC magnetization curves of a spin glass, recorded on reheating after cooling down to the lowest temperature (reference, black color) and including a halt at $T_{\text{halt}}$ for $3000$ s during the initial cooling (blue color). The dotted line marks $T_{\text{halt}}$. Akin to the ZFC $M(t)$ curves, the ZFC $M(T)$ curve recorded after the halt lies significantly below the reference one, measured on reheating without halt in the cooling, near $T_{\text{halt}}$. Due to
the nature of the spin glass phase and its ability to remember the aging at a given temperature and forget it outside a limited range around that temperature [24, 25], the "memory curve" and the reference coincide at all temperatures, away from the halt temperature. As a result, a characteristic memory dip is observed.

As seen in fig. 5, the quasicrystal displays the behavior expected for a spin glass. A memory dip is observed in the ZFC magnetization curves recorded including a halt at constant temperature during cooling. The "depth" of the memory dip increases with increasing halt time (fig. 5(a), (b)), and is observed at all temperatures below the cusp temperature $T_c \sim 4.7$ K (fig. 5(c), (d)). The $T_{\text{halt}}/T_1$ values in fig. 5(c), (d) span the 0.55−1 range. It is interesting that such sharp dips, with depths monotonously increasing as $T_{\text{halt}}$ is lowered, have been observed in metallic spin glasses in similar $T_{\text{halt}}/T_1$ ranges [ref. [16], see figs. 21 and 22]. In those "Heisenberg" systems, the isotropic glassy state stems from the RKKY interaction, and includes some unidirectional anisotropy [12, 26]. Interestingly, similar sharp dips were observed in a chiral superconductor, with Heisenberg-like behavior [12, 20]. On the contrary, the aging has been found to be more accumulative in anisotropic (Ising) spin glasses [16], as well as in superspin glasses [17] and geometrically frustrated systems [18], yielding broader memory dips. Unlike the Heisenberg systems, the depth of the memory dips in this case is almost constant below $T_1$ ([16], see fig. 21). Although there is only limited data available, it appears that the aging, memory, and rejuvenation features of XY spin glasses are similar to those of Ising ones [19] (see also [27]).

**Conclusion.** To conclude, the dynamical magnetic properties of a single crystal of the $i$-GdCd$_7$5 quasicrystal have been investigated by performing memory experiments. The quasicrystal was found to display the aging, memory, and rejuvenation features characteristic of spin glasses. The halt temperature dependence of the results suggests aging, memory, and rejuvenation features similar to those of the RKKY Heisenberg spin glasses.

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