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Heisenberg spin-glass behaviour in $Ga_{0.99}Yb_{0.01}FeO_3$

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ABSTRACT

The dynamic and static magnetic properties of $Ga_{0.99}Yb_{0.01}FeO_3$ are studied in detail using ac susceptibility and dc magnetization measurements. The study shows that the compound undergoes a spin-glass freezing at $T_g \approx 213$ K. The dynamic scaling analysis of ac susceptibility data reveals typical features characteristic of canonical spin-glasses, i.e., relaxation time $\tau^* \sim 10^{-14}$ s, critical exponent $\nu z = 4.1 \pm 0.2$, and frequency sensitivity parameter $\delta_f \sim 10^{-3}$ within three frequency decades. The analysis of the critical behaviour of the static nonlinear susceptibility yields the critical exponents $\gamma = 4.3 \pm 0.1$, $\beta = 1.0 \pm 0.1$, and $\delta = 5.5 \pm 0.5$, which lie between those typical of three-dimensional (3D) weakly anisotropic Heisenberg and Ising spin glasses. The analysis of the field-cooled and zero-field-cooled magnetization data allows to define two characteristic temperatures depending on the applied magnetic field. The upper one, $T_{irr}(H)$, is the threshold temperature corresponding to the appearance of weak irreversibility, whereas the lower one, $T_s(H)$, marks the onset of strong irreversibility. The resulting field-temperature phase diagram turns out to be in good quantitative agreement with the mean-field predictions for 3D Heisenberg spin-glass with random magnetic anisotropy, and appears consistent with the chiral driven freezing scenario.

1. Introduction

In recent years, magnetoelectric materials showing a significant coupling between electric and magnetic degrees of freedom have generated enormous research efforts because of their potential in technological developments of new spintronic devices, such as sensors and storage of data [1]. Up to now, there are few magnetoelectric materials for room temperature (RT) applications. One of the most suitable magnetoelectric materials seems to be $BiFeO_3$, for which an electric-field-induced spin flop at RT has been reported [2]. However, the ferroelectric and antiferromagnetic orders in this material are associated to different ions, yielding a weak magnetoelectric coupling.

Gallium ferrite $Ga_{2-x}Fe_xO_3$ ($0.7 \leqslant x \leqslant 1.4$), which was first synthesized by Remeika [3], appears to be also a prominent candidate of magnetoelectric materials for RT applications. Indeed, several experiments have revealed remarkable features of this material, such as piezoelectricity at RT [3,4], and the possibility of tuning the magnetic transition temperature close to or above RT depending upon x [3,5–10] and preparation conditions [5,7,11,12]. Another interesting property of this material is that its magnetic and electric orders are associated with the same type of ion, i.e. Fe^{3+}, which could lead to a rather strong magnetoelectric coupling [7,13–17]. $Ga_{2-x}Fe_xO_3$ has a non-centrosymmetric orthorhombic structure with space group $Pc2_1n$ [18]. The Fe and Ga atoms occupy three inequivalent distorted octahedral sites (Fe1, Fe2, Ga2) and one tetrahedral site (Ga1) [19]. The very small difference in the sizes of Fe^{3+}(0.64) and Ga^{3+} (0.62 Å) ions induces a cationic site disorder which plays a crucial role in the magnetic properties of this material. Recent *ab initio* calculations [20,21] and structural studies using neutron diffraction [7,9,12] on different composition of $Ga_{2-x}Fe_xO_3$, indicate that Ga/Fe site disorder is at the origin of the ferrimagnetic spin configuration observed in experiments [22]. However, magnetization measurements combined with ESR experiments revealed the presence of short-range spin–spin correlations in the paramagnetic phase of $GaFeO_3$, confirming that this material is not a classical ferrimagnet [23]. Moreover, $GaFeO_3$ was recently reported to show other interesting features such as magnetic frustration effect [24], magnetic anisotropy [25], and re-entrant spin-glass (SG) phase below the ferrimagnetic ordering temperature [26,27]. So, the nature of the magnetic ground state of $GaFeO_3$ seems to vary depending on the sample preparation, which affects the cationic site disorder [5,7,11,12].

Recently, we have synthesized high quality polycrystalline samples of $Ga_{1.99}Yb_{0.01}FeO_3$ in order to investigate the effect of the substitution of some non magnetic ions Ga^{3+} by magnetic ions Yb^{3+} on the structural parameters and magnetic properties of

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$GaFeO_3$ [28]. Notably, we found that the Yb^{3+} ions occupy mainly the site Ga2. Therefore, such a substitution of Ga by Yb atoms could result in an increase in the magnetic disorder compared to unsubstituted compound. In this paper, to the best of our knowledge, we present the first detailed study of magnetic properties of $Ga_{0.99}Yb_{0.01}FeO_3$. We observe that this system does not exhibit any long-range magnetic order down to low temperatures, in contrast to the behaviours reported for the unsubstituted compound. Indeed, we observe a single paramagnetic-SG transition on cooling, showing a magnetic field dependence similar to that of a three-dimensional (3D) Heisenberg SG.

2. Experiment

Polycrystalline samples of $Ga_{0.99}Yb_{0.01}FeO_3$ were prepared by an organic gel-assisted citrate process [29]. Solutions of gallium, iron and ytterbium nitrates were mixed in a stoichiometric ratio and chelated by adding triammonium citrate. A polyacrylamide network was formed in situ by the organic monomers consisting of acrylamide and N,N'-methylene-bis-acrylamide which were co-polymerised by heating at about 250 °C. The gel was calcined at 650 °C for 5 h, leading to a very fine powder of high chemical homogeneity of $Ga_{0.99}Yb_{0.01}FeO_3$. Then, the powder was slightly crushed and pressed isostatically under 4 kbar in the form of a cylindrical slab of about 1 cm diameter and 3 mm thickness, and sintered at 1200 °C for 24 h in air.

The crystalline structure of the obtained samples of $Ga_{0.99}Yb_{0.01}FeO_3$ were characterized by powder X-ray diffraction (XRD) measurements using a Bruker D8 diffractometer operating at room temperature with Cu $K\alpha$ radiation. The concentration of Yb was verified using energy-dispersive X-ray spectroscopy. A Rietveld analysis of the powder XRD patterns was performed using the software package Jana2006, showing that all the observed peaks can be assigned to reflections of the $Pc2_1n$ orthorhombic structure of the GaFeO system [18,30]. Moreover, no impurity phase was found. In the $Ga_{1-x}Yb_xFeO_3$ composition, the structural analysis showed that the unit cell parameters and volume increase linearly with x – indicating that the ytterbium ions enter within the structure of $GaFeO_3$ – and gave the following lattice parameter values $a = 8.7424(4)$ Å, $b = 9.3950(5)$ Å, $c = 5.0821(3)$ Å for $Ga_{0.99}Yb_{0.01}FeO_3$. We also found that the iron atoms are distributed over all the cationic sites Fe1, Fe2, Ga1, and Ga2 with occupancy rates $k_{Fe1} = 0.78, k_{Fe2} = 0.75, k_{Ga1} = 0.15$, and $k_{Ga2} = 0.32$, while the ytterbium atoms are mainly localized on the Ga2 site [28].

Measurements of the AC magnetic susceptibility and longitudinal magnetization as a function of temperature were performed using a Quantum Design PPMS system with ACMS and VSM options. The ac susceptibility measurements were made using a modulation field of 1 mT at different frequencies varying from 10 Hz to 10 kHz in the absence of any applied dc field. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were carried out using the following procedure. First, the sample is cooled to 4 K in zero field and, after a waiting time of 5 min, the magnetic field is applied to the chosen value. Then, the ZFC magnetization data are recorded with increasing temperatures with a rate of 2 K/min up to 300 K. Second, the sample is cooled to 4 K under the same applied magnetic field and the FC magnetization data are taken as a function of temperature in an identical manner to the ZFC process.

3. Results and discussion

Fig. 1(a) and (b) show the dc magnetization versus temperature for $Ga_{0.99}Yb_{0.01}FeO_3$ in applied fields of 0.1 T and 0.01 T, respectively. The pronounced inflection point of magnetization curves [Fig. 1(c)] marks the magnetic transition around ~ 212K. It is to be noted that the rather narrow width of this transition, $\Delta T \approx 5$ K, obtained as the temperature interval between the two extrema of d^2M/dT^2 calculated from the FC curves for $\mu_0 H = 0.01$ T and 0.1 T [Fig. 1(d)], provides an indication of the high quality of the sample.

A bifurcation between M_{ZFC} and M_{FC} marks the onset of magnetic irreversibility below a certain temperature T_{irr} which decreases with increasing field (see below). Another significant feature clearly visible in Fig. 1(a) and (b) is the peak at a certain temperature $T_p < T_{irr}$ in the ZFC curves, which broadens and shifts toward lower temperatures when the field increases. Note that such features revealing nonequilibrium behaviours was also observed in $GaFeO_3$ [8,12,23,24,26,27].

On the other hand, Fig. 2 shows a few representative Arrot plots [31] (i.e., M^2 versus H/M) obtained from FC magnetization isotherms at different temperatures below the magnetic transition. We see that the Arrott plots show a clear curvature downward and intersect the H/M axis. This clearly indicates no sign of spontaneous magnetization and, therefore, reveals the existence of a short-range magnetic order down to low temperatures.

These irreversible effects and the existence of a short-range ordering suggest the freezing of the Fe/Yb magnetic moments into a glassy state below ~ 212 K. However, it should be stressed that theses features do not constitute a sufficient condition to conclude that $Ga_{0.99}Yb_{0.01}FeO_3$ displays a SG transition as they should also be observed in the alternative scenario that assumes the existence of some inhomogeneous ferrimagnetic clusters. Thus, in the following paragraphs, we present a detailed study of the static and dynamic magnetic properties of $Ga_{0.99}Yb_{0.01}FeO_3$ which allows to establish the nature of its low-temperature magnetic phase.

3.1. ac susceptibility

Fig. 3 shows the temperature dependence of the real (in-phase), χ', and imaginary (out-of-phase), χ'', parts of the ac magnetic susceptibility χ. They have been measured during warming up in zero dc magnetic field by applying a modulation magnetic field of 1.0 mT at different frequencies varying from $f = 10$ Hz to 10 kHz. $\chi'(T)$ exhibits a marked maximum at T_f which roughly coincides with the maximum of $|d\chi''(T)/dT|$, i.e. the inflection point in the jump of $\chi''(T)$. At larger temperatures above T_f, $\chi''(T)$ is equal to zero, whereas below T_f it has a finite value lower than that of $\chi'(T)$. Fig. 3(a) shows that the position, T_f, of the maximum of $\chi'(T)$ shifts toward higher temperatures with increasing frequency. In addition, χ' decreases as the frequency increases, whereas it becomes independent of frequency concomitantly with the vanishing of χ''. Such a behaviour of χ' and χ'' is a typical characteristic of the SG-like systems.

The relative variation of T_f per decade of frequency [32]:

$$\delta_f = \frac{\Delta T_f}{T_f \Delta \log_{10} f} \tag{1}$$

is a parameter often used to compare the sensitivity to frequency variations of the different types of SG-like systems. The values of δ_f are typically of the order of 10^{-3} for metallic SG (e.g., $\delta_f \approx 0.0050$ for CuMn alloys [33]) to 10^{-2} for insulating SG (e.g., $\delta_f \approx 0.02$ for $Eu_{0.4}Sr_{0.6}S$ [34]) and cluster glasses, i.e., systems with random weak interactions between magnetic clusters rather than individual spins (e.g., $\delta_f \approx 0.06$ for Fe-Al_2O_3 particles [35]). For superparamagnetic-like-systems, i.e., systems consisting of isolated magnetic entities, values of δ_f of the order of 0.1 are measured (e.g., $\delta_f \approx 0.13$ for $La_{0.994}Gd_{0.006}Al_2$ [36]).