Observation of enhanced Magnetic Transition in Pbnm SmFeO$_3$

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Abstract:

Rare-earth orthoferrites RFeO$_3$ materials have recently attracted a great attention for their intriguing physical properties, ideal for numerous technological applications, such as ultrafast photo-magnetic recording [1-4], inertia-driven spin switching [5], laser-induced ultrafast spin reorientation [6-7], magnetic biasing on P-E hysteresis loops [8], enhanced magnetoelectric interactions [9,10], multiferroics, ferroelectrics [11-15]. The family of RMO$_3$ materials is generally characterized by a distorted perovskite Pbnm structure which exhibits a weak ferromagnetic behavior due to a small canting of the antiferromagnetic metal sub-lattices (M$^{3+}$-sub-lattices). In these structures two magnetic sub-lattices can be identified: one due to the 4f-electrons of the rare-earth ions (R-sub-lattice) and another due to the 3d-electrons of the Fe ions (Fe-sub-lattice) [16-21]. One of the most attractive properties of RMO$_3$ materials is the spin reorientation (SR). SR is a phenomenon which can be induced by temperature and/or by an applied magnetic field. In this type of effect the direction of the easy axis of magnetization has been reported to change from one crystal axis to

Introduction

Rare-earth orthoferrites $R$FeO$_3$ ($R$= rare-earth ion) materials have recently attracted a great attention for their intriguing physical properties, ideal for numerous technological applications, such as ultrafast photo-magnetic recording [1-4], inertia-driven spin switching [5], laser-induced ultrafast spin reorientation [6-7], magnetic biasing on P-E hysteresis loops [8], enhanced magnetoelectric interactions [9,10], multiferroics, ferroelectrics [11-15]. The family of RMO$_3$ materials is generally characterized by a distorted perovskite Pbnm structure which exhibits a weak ferromagnetic behavior due to a small canting of the antiferromagnetic metal sub-lattices (M$^{3+}$-sub-lattices). In these structures two magnetic sub-lattices can be identified: one due to the 4f-electrons of the rare-earth ions (R-sub-lattice) and another due to the 3d-electrons of the Fe ions (Fe-sub-lattice) [16-21]. One of the most attractive properties of RMO$_3$ materials is the spin reorientation (SR). SR is a phenomenon which can be induced by temperature and/or by an applied magnetic field. In this type of effect the direction of the easy axis of magnetization has been reported to change from one crystal axis to
another with the change of temperature and/or
applied magnetic field parameters [15,16,20,21].
Previous works have attributed the origin of SR to
antisymmetric (as described by Dzyaloshinskii
[22], Moriya [23], and Treves [24]) and
anisotropic-symmetric exchange interactions
between Metal (M3+) and Rare-Earth (R3+)
magnetic moments [21].

The observed spin configurations and the SR
dynamics in RMO3 are generally classified into 3
configurations, following the Bertaut description,
namely \( \Gamma_1 \), \( \Gamma_2 \) and \( \Gamma_4 \) [16]. Among many RFeO3
materials, SmFeO3 has recently attracted a great
attention not only for the excellent physical
properties such as 1) fast magnetic switching, and
2) easy axis rotation transition (also known as spin
reorientation transition) but also for its newly
observed room-temperature ferroelectric
properties [11-15]. In this type of materials the SR
effect involves two main spin configurations,
namely \( \Gamma_4 \) at high temperature and \( \Gamma_2 \) at low
temperature [15,16]. These configurations are
defined by the symbols \( \Gamma_4 \) (\( G_x \), \( A_y \), \( F_z \)) and \( \Gamma_2 \) (\( F_x \),
\( C_y \), \( G_z \)) [21].

In these spin configurations \( G_x \) represents the
antiferromagnetic spin-configuration of the metal
M3+ ions along the a-axis and \( F_z \) the ferromagnetic
spin-configuration along the c-axis. \( A_y \) represents
the antiferromagnetic-spin-arrangement along the
b-axis (due to hidden canting of \( G_x \) spins) [21].

The dynamics of the temperature induced SR in
this type of material can be explained as follow: as
the temperature is lowered, the easy axis of
magnetization begins to rotate at a temperature \( T_2 \),
and ceases to rotate when the rotation angle
reaches 90 degrees at another temperature \( T_1 \),
resulting in spin-configuration \( \Gamma_2 \) (\( F_x \), \( C_y \), \( G_z \))
where \( C_y \) represents another hidden canting
spin-configuration [21]. Particularly the dynamics
of SR are being recently re-investigated due to
possible important correlations of this phenomenon with magnetically driven
ferroelectricity effects [11-15].

Recent works have indeed reported the discovery
of ferroelectric polarization in SmFeO3 below 670
K (Neel Temperature). The origin of this
ferroelectric polarization is highly debated and
still not well understood [11-14]. An inverse
Dzyaloshinskii-Moriya interaction based
mechanism was firstly reported to be the driving
force of such ferroelectric properties [11].
However this interpretation was very recently
revised due to incompatibilities in the calculated
\( k = 0 \) magnetic structure, which could not be
responsible for the spin-orbit-coupling driven
ferroelectric polarization by \( S_i \times S_j \) (due to
un-broken inversion symmetry) [12]. Thus an
alternative mechanism based on JS \( \cdot S_j \)
exchange-striction was then proposed [13]. Such
interpretation is still debated and not confirmed by
other very recent investigations, where no
ferroelectricity has been found in single crystals of
the same material (SmFeO3) [14].

In this work we continue to investigate the
fascinating physical properties of SmFeO3
materials focusing our attention on T-dependent
Zero Field Cooled (ZFC) and Field Cooled (FC)
magnetization properties of micrometer scale
crystals obtained by annealing methods.

Particularly, we report the observation of a not
previously reported magnetic transition at the
temperature of approximately 139 K. From
literature bulk susceptibility measurements, is has
been suggested that below the temperature of
about 140 K, Sm3+ moments would begin to order
antiparallel to the Fe-moments due to
antiferromagnetic f-d exchange interactions. We
therefore attribute the observed transition to
compensation effects induced by the appearance
of long range ordering in Sm3+ ions. The
magnetic-nature of the observed transition is
confirmed by additional temperature dependent
Powder X-ray Diffraction analysis which did not
show structural changes in the same temperature
range (from 298 K to 100 K). Due to residual
small fractions of ferromagnetic \( \alpha \)-Fe from the
sample-growth, possible interactions between the
magnetic moment of \( \alpha \)-Fe and the SmFeO3
crystals at the compensation temperature can not
be excluded. However, no exchange-bias effects
Experimental:
The SmFeO$_3$ crystals were prepared by annealing mixtures of Fe-filled carbon foam (produced with the method reported in ref.[26]) and Sm$_2$O$_3$ nanoparticles in an Ar and Ar/H$_2$ flow of 15 ml/min within a chemical vapour deposition system consisting of a quartz tube reactor and an electrical furnace set at the temperature of approximately 990 °C. Transmission electron microscopy (TEM) and Scanning TEM (STEM) investigations were performed by using a 200 kV American FEI Tecnai G$^2$F20 fitted with field emission gun. Variable temperature XRD analysis was performed with a Panalytical Empyrean powder diffractometer (Cu K-α with λ = 0.154 nm) equipped with a primary Johansson monochromator, an Oxford Cryosystems PhoeniX cryostat, and a X’celerator linear detector. The magnetic measurements (zero field cooled (ZFC), field cooled (FC) and hysteresis loops) were performed by employing a VSM Quantum Design and a VSM Cryogenic Limited London UK.

Results and Discussion
The morphology of the as annealed SmFeO$_3$ crystals was revealed by TEM performed in STEM mode. Due to the high thickness of the crystals, the use of STEM atomic contrast was used for a better visualization of the cross-sectional morphology of the grown crystals. In particular the brighter areas in Fig.1 represent the SmFeO$_3$ phase. Note also the presence of small flakes of grey-like areas which could be associated to residual α-Fe-filled carbon foam not completely oxidized during the annealing process.

The presence of $Pbnm$ SmFeO$_3$ crystals within the post-annealed sample was further confirmed by room temperature XRD, as shown in Fig.2. Together with the presence of intense crystalline peaks of SmFeO$_3$, the presence of a residual α-Fe phase was confirmed by the observation of the 110 reflection.

The attention was then turned on the magnetic properties of the produced samples. The presence of a magnetic transition in the temperature range
From 100 K to 200 K was firstly revealed by ZFC measurements as shown in Fig.3.

The existence of such magnetic transition was also confirmed by further FC measurements performed at different fields. Fig.4 shows the typical result of an FC measurement at the applied field of 300 Oe. Furthermore Figs.5-6 show the results of FC measurements at 500 Oe and 800 Oe respectively. It is important to notice that the observed peak is found to become clearer with the increase of the magnetic field used for the FC measurement.

The observation of this transition cannot be explained on the basis of the previously observed SR phenomenon, which has been generally reported at the temperature in the order of 480 K. Indeed, below the Neel temperature, near 670 K, the weak ferromagnetic moments (associated to the Fe-sublattice spins of the SmFeO$_3$ phase) are expected to re-orient from the c-axis towards the a-axis. It has been shown that this effect observed at approximately 480 K causes the c-axis susceptibility to decrease rapidly below this temperature, and simultaneously, the a-axis susceptibility to rise sharply [25]. Furthermore, the observed transition is not compatible with possible exchange bias effects, since no unusual magnetization or coercivity shifts in the hysteresis loops were found at different temperatures as shown in Fig.7A-B and Fig.8. Note however that in our samples the hysteresis loops magnetization-dynamics may be influenced by the ferromagnetic behavior of the residual $\alpha$-Fe component mentioned above (see also Supp. Info.Figs.1-10).
Instead, considering the low temperature magnetic properties of SmFeO$_3$, an important observation can be made. Indeed at cryogenic temperatures, the magnetization of SmFeO$_3$ has been reported to exhibit a spontaneous magnetization reversal [15,17,18,19,25]. This reversal has been previously attributed to a compensation effect of the weak ferromagnetic moment (associated to the Fe-sublattice spins of the SmFeO$_3$ phase) by antiparallel alignment of the Sm$^{3+}$ moments. Additionally from the bulk susceptibility it has been suggested that below the temperature of about 140 K, Sm$^{3+}$ moments would begin to order antiparallel to the Fe-moments due to antiferromagnetic f-d exchange interactions between the two magnetic sub-lattices [25]. Interestingly, recent measurements by Y. K. Jeong et al. [19] revealed a change in the slope of the magnetization curves in their FC measurements from the temperature of approximately 135 K; but no clear magnetization peak was reported. However, it is important to notice that such temperature range is compatible with that observed in our measurements shown in Figs.3-6. Therefore a notable role of the α-Fe ferromagnetic phase on such enhancement of the magnetic transition signal cannot be excluded.

In the attempt to further confirm the magnetic nature of the observed transition, and therefore exclude possible structural changes within the samples, temperature dependent XRD was carried out. As shown in Figs.9-10 no changes in the structure of the SmFeO$_3$ and α-Fe phases were found in the XRD measurements performed in the temperature range from 298 K to 100 K. These results confirm the interpretations above and suggest that the observed transition in the temperature range between 130 K and 140 K is of magnetic-nature and can be attributed to compensation effects of the ferromagnetic Fe-sublattice moments by antiparallel alignment with the Sm$^{3+}$ moments. This is also confirmed by the fact that Sm$^{3+}$ spins are expected to undergo...
long-range ordering from temperatures in the order of 140 K.

However future studies will clarify a possible role of the residual \( \alpha \)-Fe phase in such magnetic transition and its possible interaction with the Sm\(^{3+} \) moments of the SmFeO\(_3 \) phase.

Conclusion

In conclusion we reported the direct observation of enhanced compensation effects by ZFC and FC measurements of micrometer-scale SmFeO\(_3 \) crystals obtained by direct high temperature annealing of Fe-filled carbon foam and Sm\(_2\)O\(_3 \) nanoparticles mixtures in Ar and Ar/H\(_2 \) flow. The magnetic nature of the transition was also confirmed by additional temperature dependent XRD which did not show structural changes of the sample in the temperature range from 298 K to 100 K.

Supplementary Material

See supplementary online material for Rietveld Refinement analyses of different portions of the as grown powder sample and detailed calculations and measurements of the \( \alpha \)-Fe contribution to the magnetization in the case of 1) the only carbon foam filled with \( \alpha \)-Fe (before the annealing stage) and 2) the \( \alpha \)-Fe-foam/SmFeO\(_3 \) crystals reported in this work. Additional SEM images of the SmFeO\(_3 \) crystals are also shown.

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References
