Magnetic memory effect in multiferroic K3Fe5F15 and K3Cr2Fe3F15

Jagličić, Zvonko; Pajić, Damir; Trontelj, Zvonko; Dolinšek, Janez

Applied Physics Letters

Magnetic memory effect in multiferroic K3Fe5F15 and K3Cr2Fe3F15

Z. Jagličić, D. Pajić, Z. Trontelj, J. Dolinšek, and M. Jagodič

Citation: Appl. Phys. Lett. **102**, 242410 (2013); doi: 10.1063/1.4811762
View online: http://dx.doi.org/10.1063/1.4811762
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i24
Published by the AIP Publishing LLC.

APPLIED PHYSICS LETTERS **102**, 242410 (2013)

Magnetic memory effect in multiferroic $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$

Z. Jagličić,[1,2] D. Pajić,[3] Z. Trontelj,[1] J. Dolinšek,[4,5] and M. Jagodič[1]
[1]*Institute of Mathematics, Physics and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia*
[2]*Faculty of Civil and Geodetic Engineering, University of Ljubljana, Jamova 2, 1000 Ljubljana, Slovenia*
[3]*Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, 10000 Zagreb, Croatia*
[4]*Jožef Stefan Institute, University of Ljubljana, Jamova 39, SI-1000 Ljubljana, Slovenia*
[5]*EN-FIST Centre of Excellence, Dunajska 156, SI-1000 Ljubljana, Slovenia*

(Received 8 May 2013; accepted 5 June 2013; published online 19 June 2013)

The fluorides $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ are known as multiferroic materials. Here we report the detection of a magnetic memory effect in these materials and its dependence on temperature and aging time. We succeeded in writing, reading, and deleting 3-bits digital information in these systems. These results show that in addition to their already known magneto-electric multiferroic properties, $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ also possess a new functionality: they can be used as materials for a thermal memory cell. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4811762]

Multiferroic materials combine both ferromagnetic and ferroelectric properties in one system, thus achieving a rich functionality.[1,2] The vast majority of all known inorganic ferroelectrics and multiferroics are oxides like $BiFeO_3$,[3] the best known example. Although much effort has been put into research on multiferroic oxide materials, coupling between the magnetic and electric properties is still relatively weak, and there are many unsolved questions about the nature of this coupling. These are the main reasons for looking for multiferroic properties in other, non-oxide materials. By substituting oxygen with fluorine a new family of multiferroic materials has recently been reported.[4,5] These new fluorides can be represented by the formula $K_3M_3^{2+}M_2^{3+}F_{15}$ where M denotes a transition metal (Fe, Mn, Co, Cr) with the orthorhombically deformed tetragonal tungsten bronze structure.[6,7] While the ferroelectric transitions occur well above room temperature in these materials (for example $T_c = 490$ K for $K_3Fe_5F_{15}$ (Ref. 8), the magnetic phase transitions occur below room temperature. For $K_3Fe_5F_{15}$ a magnetic transition at 122 K has been found,[4] while for $K_3Cr_2Fe_3F_{15}$ two magnetic glass-like transitions at 35 and 17 K have been reported.[5] Below the transition temperatures (122 K and 35 K for $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$, respectively), a large difference between the zero-field-cooled and field-cooled magnetic susceptibilities has been observed. Slow magnetic dynamics in both systems has been measured and described in detail[9] confirming the non-ergodic magnetic behaviour of the systems at low temperature. In addition, muon spin relaxation measurements in $K_3Cr_2Fe_3F_{15}$ suggest that the system is inhomogeneous below 35 K, with magnetically ordered clusters being embedded in a disordered matrix.[10]

One of the most spectacular manifestations of slow magnetic relaxation and non-ergodicity in a system is the magnetic memory effect. It has recently been shown that the magnetic memory effect can be utilized for digital information storage in a *thermal memory cell*.[11] The magnetic memory effect is a phenomenon that occurs in materials with broken ergodicity. Such materials are able to remember their thermal history. During an experiment the sample is cooled down in zero magnetic field from high temperature to a temperature below the phase transition to the non-ergodic phase. At a particular temperature or even at several subsequent temperatures in the non-ergodic phase the cooling is stopped, leaving the system to age for an aging time ranging from a few minutes up to several hours. Finally, the sample is cooled down to the lowest temperature, and its magnetization is measured upon heating in a small magnetic field of a few Oersteds. At the aging temperatures small dips in the magnetization can be observed. In this way a one-to-one correspondence between a stop or non-stop at a particular temperature (=writing procedure) and the detection or non-detection of a dip at the same temperature upon heating (=reading procedure) can be established and associated with a bit or byte of information. By choosing a desired sequence of stopping (aging) temperatures, an arbitrary character from the ACSII code system has been imprinted into two systems in the non-ergodic phase: a Cu-Mn canonical spin glass and a Taylor-phase T-Al_3(Mn,Fe) complex intermetallic compound.[12] The extensive physical background of the memory effect and the conditions necessary to observe a memory effect were described in Ref. 13, and examples of systems where it can be observed are spin glasses,[14] geometrically frustrated antiferromagnets,[15] and magnetic nanoparticles.[16]

In the present work detection of the memory effect in multiferroic $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ is reported, and its dependence on temperature and aging time is investigated. Using a magnetic memory effect 3-bits information was written, read, and deleted in these systems.

Polycrystalline samples of $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ were prepared as described in Refs. 4 and 5. The crystal structures of the prepared compounds were confirmed by X-ray analysis to be in accordance with the published data.[6]

Magnetization measurements were performed on a Quantum Design MPMS-XL-5 SQUID magnetometer equipped with a 5 T superconductive magnet and operating in the temperature range of 1.9–400 K.

The same samples were used as in already published works.[5,9] The zero-field-cooled, field-cooled, and ac susceptibility measurements were repeated. The measured magnetic properties were identical to the ones in above-mentioned references, thus confirming the quality of the samples.

In Fig. 1 a typical magnetic memory effect and the inscription of digital information into $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ is shown. To obtain a reference curve the sample was first cooled down from 150 K to 2 K at a cooling rate of 2 K/min in zero magnetic field. At 2 K a magnetic field $H_r = 4$ Oe (subscript "r" stands for "reading") was switched on and the magnetization measured upon heating the sample at a heating rate of 0.3 K/min. The magnetization obtained is shown as the upper/black line in Figs. 1(a) and 1(b). In the next step the sample was cooled down again from 150 K in zero magnetic field, but now the cooling was stopped at three temperatures, namely, at 90 K, 60 K, and 30 K for $K_3Fe_5F_{15}$ and at 30 K, 20 K, and 10 K for $K_3Cr_2Fe_3F_{15}$, leaving the sample to "age" isothermally for one hour (aging or waiting time $t_w = 1$ h) at each temperature. Finally, at 2 K a magnetic field $H_r = 4$ Oe was switched on, and the magnetization was measured while heating the sample at the same temperature rate as for the reference curve. The magnetizations observed are shown as the green lines in Figs. 1(a) and 1(b), shifted by 0.5×10^{-3} emu/g downward so as not to overlap with the reference curves. Non-distinctive dips appear at the stopping temperatures in the measured magnetization, almost invisible to the naked eye (shown on the graphs in Figs. 1(a) and 1(b)). The memory effect is much less pronounced in $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ than for example in canonical spin glasses[11] but is comparable to superparamagnetic systems.[17] However, when calculating the difference ΔM between the reference curve and the magnetization obtained after aging the sample (Figs. 1(c) and 1(d)), three distinctive dips appear on each graph at the stopping temperatures, showing that the multiferroic $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$ can be used as the materials for thermal memory cell.

In order to obtain deeper insight into the nature of the magnetic state in the multiferroic fluorides of the $K_3M_3^{II}M_2^{III}F_{15}$ family and to compare their magnetic properties with the properties of other non-ergodic systems exhibiting a magnetic memory effect, we studied the influence of aging time t_w on the amplitude of the memory effect ΔM. As ΔM is larger in $K_3Cr_2Fe_3F_{15}$, we show only the results obtained for this compound.

Figure 2 shows the memory effect in $K_3Cr_2Fe_3F_{15}$ at three temperatures (10 K, 20 K, and 30 K) for different aging times t_w spanning a range from 10 min up to 4 h. The amplitude of the memory effect ΔM_{max} increases with aging time for all three chosen stopping temperatures. At temperatures of 10 K and 30 K the memory effect is already observable after only 10 min of aging of the sample and saturates after approximately 2 h of aging time. A similar dependence of ΔM_{max} vs. t_w as shown on the graph in Fig. 2(b) was obtained in Taylor-phase Al_3(Mn, Pd, Fe) complex intermetallics.[13]

The amplitude ΔM at 20 K is much smaller than the memory effect at 10 K and 30 K, regardless of the aging time t_w. This result at first glance seems unusual when compared to some other magnetically frustrated systems like, for example, Taylor-phase Al_3(Mn, Pd, Fe) complex intermetallics,[13] or the strong phase competition system $La_{0.7}Ca_{0.3}Mn_{0.925}Ti_{0.075}O_3$,[18] where the amplitude of the memory effect ΔM shows a "resonant" curve with a maximum at a temperature that is approximately one half of the transition temperature in the corresponding system. The memory effect observed in $K_3Cr_2Fe_3F_{15}$ with the smallest amplitude ΔM at 20 K, which is approximately in the middle of the non-ergodic temperature interval (between 1.9 K and 37 K), can be understood in relation to the two magnetic transitions at 37 K and 17 K in $K_3Cr_2Fe_3F_{15}$. It is in full agreement with the two maxima detected in the temperature dependence of the logarithmic relaxation rate associated with the activation of two different groups of magnetic moments with well separated energy barriers.[9]

We have shown that it is possible to **write**, i.e., age at a particular stopping temperature, and to **read**, i.e., observe dips in the measured magnetization during heating the sample, digital information into and out of the multiferroic systems $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$. Finally, we succeeded in

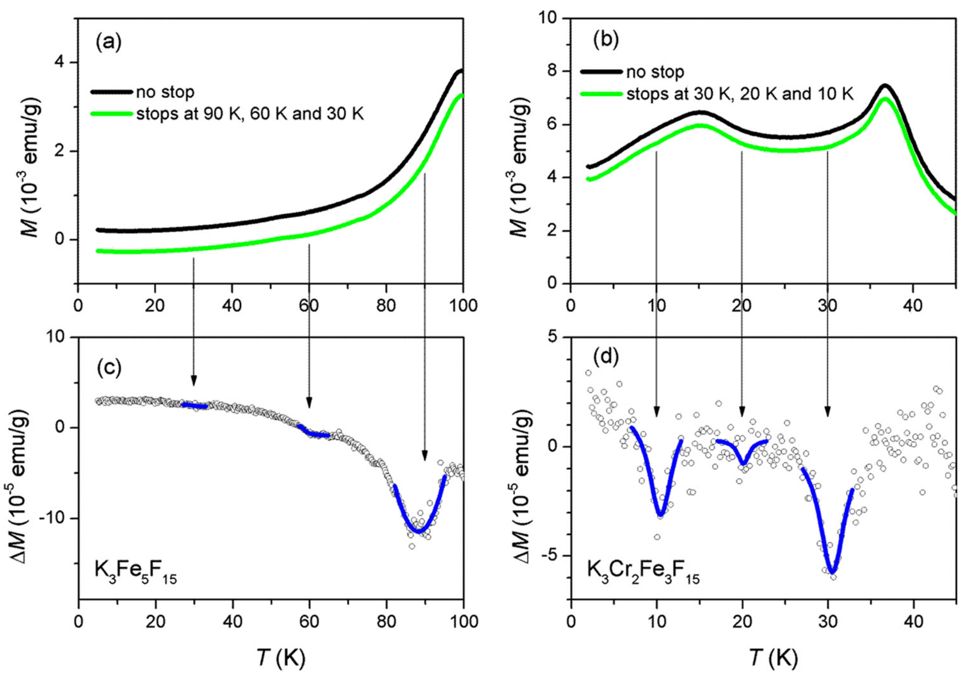

FIG. 1. Magnetic memory effect in $K_3Fe_5F_{15}$ (left panels (a) and (c)) and $K_3Cr_2Fe_3F_{15}$ (right panels (b) and (d)). The magnetic field during reading was $H_r = 4$ Oe for both samples, and the stopping temperatures are shown by arrows. The full lines in graphs (c) and (d) serve only as guides to the eye.

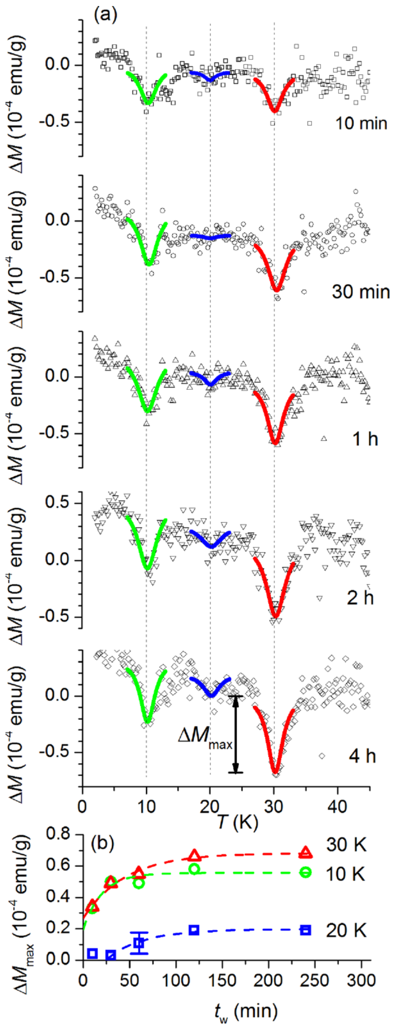

FIG. 2. Memory effect ΔM as a function of waiting time t_w in $K_3Cr_2Fe_3F_{15}$ at 10 K, 20 K, and 30 K. (a) The reading field was $H_r = 4$ Oe. The amplitude of the memory effect ΔM_{max} is plotted versus the waiting time t_w (b).

deleting the information stored in the material, and in this way confirmed that it can be used as a thermal memory cell. For demonstration purposes we used the $K_3Cr_2Fe_3F_{15}$ sample. First we wrote down the information by aging the sample at 30 K, 20 K, and 10 K during the cooling procedure. In this way we wrote three bits of information into the system, all presenting a logical "1." To read this information we heated the material and simultaneously measured the magnetization in a small magnetic field. The signal obtained is shown in Fig. 3, lower/green curve. The three dips at the stopping temperatures correspond to the 3-bit information "111." However, if we were to heat the sample before reading the information stored in the thermal memory cell, in zero magnetic field, the stored information could be changed. In the experiment shown in Fig. 3 the sample was heated up to 22 K after cooling and aging at 30 K, 20 K, and 10 K and then again continuously cooled down to 2 K without aging at 20 K or 10 K. In this way the signals (bits) at 10 K and 20 K were deleted. Indeed, after switching on the magnetic field H_r and reading the information stored in the thermal memory cell by measuring the magnetization upon heating the sample, there were no dips at 10 K and 20 K as shown in Fig. 3, upper/red curve. Only the dip at 30 K remained preserved

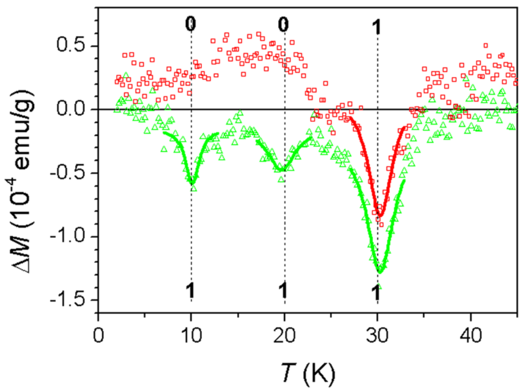

FIG. 3. Three-bit information "111" (lower/green curve) written into $K_3Cr_2Fe_3F_{15}$ and another 3-bit information "001" (upper/red curve shifted upward by 5×10^{-5} emu to prevent the two curves from overlapping) after deleting the first two bits. The reading magnetic field was $H_r = 8$ Oe.

since it was not affected by heating the sample up to 22 K. In this way we succeeded in deleting the first two bits of original information stored in the thermal memory cell and changed the "111" into "001."

In summary, the magnetic memory effect was observed for the first time in two multiferroic polycrystals, namely, $K_3Fe_5F_{15}$ and $K_3Cr_2Fe_3F_{15}$. Two important conclusions can be drawn from our detailed description of the memory effect as a function of aging time and temperature:

(a) As the effect is expected to appear only in non-ergodic magnetic systems, the detection of the memory effect itself means that the magnetic ground state in these systems cannot be a complete long-range ordered magnetic state. The memory effect is smaller in $K_3Fe_5F_{15}$ suggesting that only a small portion of the total magnetic moments in the structure contribute to this non-ergodic phenomenon and most of the magnetic moments are long-range ordered. On the other hand, the temperature-dependent amplitude of the memory effect in $K_3Cr_2Fe_3F_{15}$, with its minimum at 20 K and a larger effect at 10 K and 30 K, confirms the existence of two groups of magnetic moments with different activation energies.

(b) Multiferroic fluorides can be used as materials for a thermal memory cell. We succeeded in writing, reading and deleting bits of digital information by purely thermal manipulation of the material. In this way the memory effect and its practical application as a thermal memory cell demonstrates a new functionality of these multiferroic materials.

[1]D. I. Khomskii, J. Magn. Magn. Mater. **306**, 1 (2006).
[2]J. M. D. Coey, *Magnetism and Magnetic Materials* (Cambridge University Press, Cambridge, UK, 2010).
[3]G. Catalan and J. F. Scott, Adv. Mater. **21**, 2463 (2009).
[4]R. Blinc, G. Tavčar, B. Žemva, D. Hanžel, P. Cevc, C. Filipič, A. Levstik, Z. Jagličić, Z. Trontelj, and N. Dalal, J. Appl. Phys. **103**, 074114 (2008).
[5]R. Blinc, P. Cevc, A. Potočnik, B. Zemva, E. Goreshnik, D. Hanžel, A. Gregorovič, Z. Trontelj, Z. Jagličić, V. Laguta, M. Perović, N. S. Dalal, and J. F. Scott, J. Appl. Phys. **107**, 043511 (2010).
[6]A.-M. Hardy, A. Hardy, and G. Ferey, Acta Cryst. B **29**, 1654 (1973).
[7]J. F. Scott and R. Blinc, J. Phys.: Condens. Matter **23**, 113202 (2011).
[8]J. Ravez, S. C. Abrahams, and R. de Pape, J. Appl. Phys. **65**, 3987 (1989).
[9]D. Pajić, Z. Jagličić, R. Blinc, and Z. Trontelj, J. Appl. Phys. **112**, 073908 (2012).

[10]A. Potočnik, A. Zorko, D. Areon, E. Goreshnik, B. Žemva, R. Blinc, P. Cevc, Z. Trontelj, Z. Jaglieia, and J. F. Scott, Phys. Rev. B **81**, 214420 (2010).
[11]J. Dolinšek, M. Feuerbacher, M. Jagodič, Z. Jagličić, M. Heggen, and K. Urban, J. Appl. Phys. **106**, 043917 (2009).
[12]M. Feuerbacher, J. Dolišek, M. Heggen, Z. Jagličić, and M. Jagodič, "Verfahren zur speicherung digitaler information nebst speicherelement," *Europäische Patentanmeldung: EP 2 207 177 A2: Anmeldenummer 09179123.6.*, 2009.
[13]J. Dolinšek, J. Slanovec, Z. Jagličić, M. Heggen, S. Balanetskyy, M. Feuerbacher, and K. Urban, Phys. Rev. B **77**, 064430-1 (2008).
[14]J. P. Bouchaud, V. Dupuis, J. Hammann, and E. Vincent, Phys. Rev. B **65**, 024439 (2001).
[15]B. D. Gaulin, J. N. Reimers, T. E. Mason, J. E. Greedan, and Z. Tun, Phys. Rev. Lett. **69**, 3244 (1992).
[16]P. Jönsson, M. F. Hansen, and P. Nordblad, Phys. Rev. B **61**, 1261 (2000).
[17]T. Zhang, X. G. Li, X. P. Wang, Q. F. Fang, and M. Dressel, Eur. Phys. J. B **74**, 309 (2010).
[18]N. C. Thuan, D. N. H. Nam, N. X. Phuc, N. T. Y. Mai, L. Van Hong, N. Van Dai, V. D. Lam, and Y. P. Lee, J. Phys.: Conf. Series **187**, 012068 (2009).