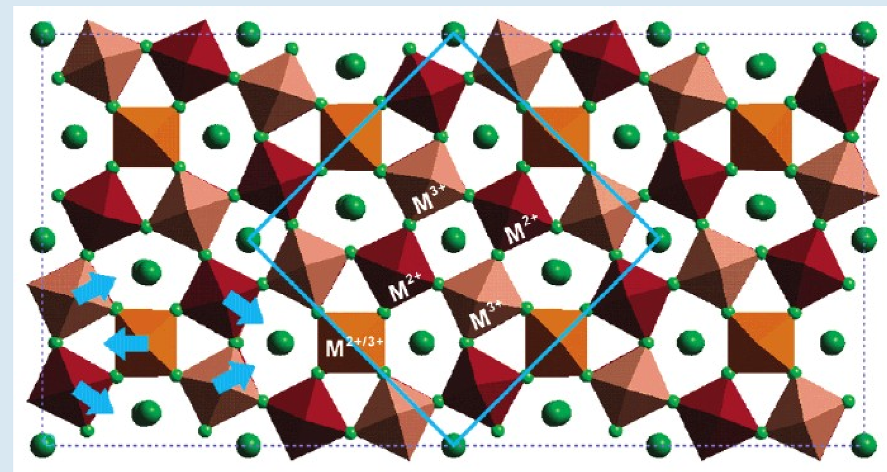
Magnetic dynamics in $K_3Fe_5F_{15}$ family of multiferroics

Damir Pajić[1,2], Zvonko Jagličić[1,3], Boris Žemva[4], Robert Blinc[4], Zvonko Trontelj[1]

[1] Institute for Mathematics, Physics and Mechanics, Ljubljana, Slovenia
[2] Department of Physics, Faculty of Science, University of Zagreb, Croatia
[3] Faculty of Civil and Geodetic Engineering, University of Ljubljana, Slovenia
[4] Jožef Stefan Institute, Ljubljana, Slovenia

Introduction and Motivation

- Magnetoelectric multiferroics are of great interest in solid state physics [1] because of coexistence of magnetic and electric order and their coupling [2]. Besides the well known perovskite oxides [3], a novel class of multiferroics are the orthorhombically deformed tetragonal tungsten bronze fluorides [4,5,6]. We continue the study of previously investigated $K_3Fe_5F_{15}$ [7], $K_3Fe_3Cr_2F_{15}$ [8] and $K_3Cu_3Fe_2F_{15}$ [9].
- Magnetic order in similar fluorides is a controversial topic, smearing over ferrimagnetism, weak (anti)ferromagnetism, spin glass disorder, short range order, geometrical frustration, … Magnetic structure of $K_3Fe_5F_{15}$, $K_3Fe_3Cr_2F_{15}$ and $K_3Cu_3Fe_2F_{15}$ is still unknown. Due to the drastically different magnetic properties between $K_3Fe_5F_{15}$, $K_3Fe_3Cr_2F_{15}$ and $K_3Cu_3Fe_2F_{15}$ we performed the detailed investigation of magnetic dynamics through the studying of relaxation of the magnetization after change of the field and temperature.

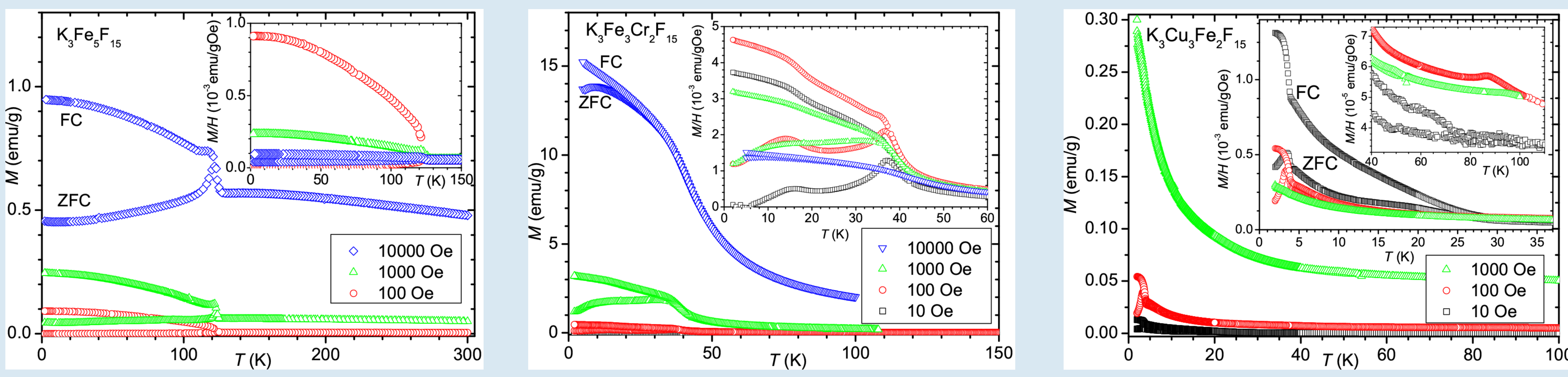


Model of the real structure to which belong our systems $K_3Fe_5F_{15}$, $K_3Fe_3Cr_2F_{15}$ and $K_3Cu_3Fe_2F_{15}$ [6].
Modulated tilting of the fluorine apical atoms designated by arrows is important for ferroelectricity, as well as for charge ordered supercell. Together with observed magnetic ordering, this enabled to construct multiferroic phase diagram [10].

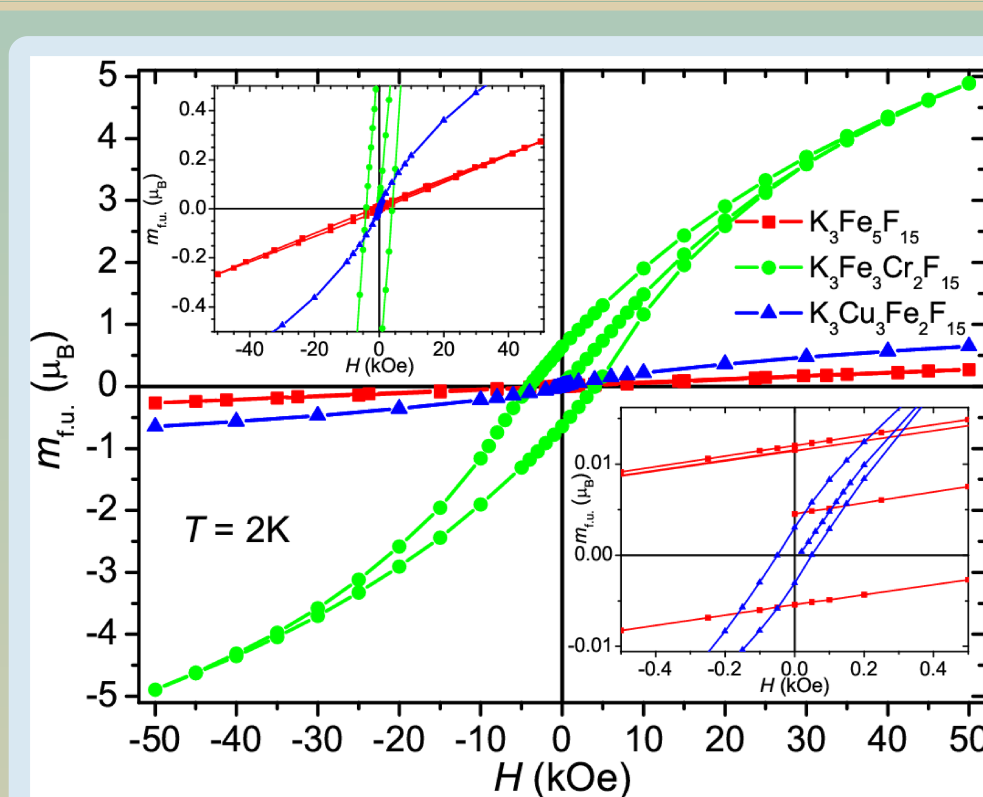
Experiments performed

- Measurement of magnetization was performed using Q.D. MPMS 5XL SQUID magnetometer in CMag laboratory.
- Temperature dependence of magnetization $M(T)$ in applied magnetic field H after zero field cooling (ZFC) and after field cooling (FC).
- Magnetic hysteresis loops $M(H)$ with maximum field of 5T.
- Change of magnetization with increasing temperature after the change of magnetic field, so called thermoremanent magnetization.
- AC magnetic susceptibility.
- Magnetic relaxation was measured as follows:
  (1) heat the sample above transition temperature
  (2) apply magnetic field H
  (3) cool down to desired temperature T
  (4) change magnetic field to $-H$
  (5) measure magnetization during one hour

Diversity of magnetic transitions in $K_3F_5F_{15}$ family



Temperature dependence of magnetization $M(T)$ in different applied magnetic fields after zero-field cooling (ZFC) and field cooling (FC).

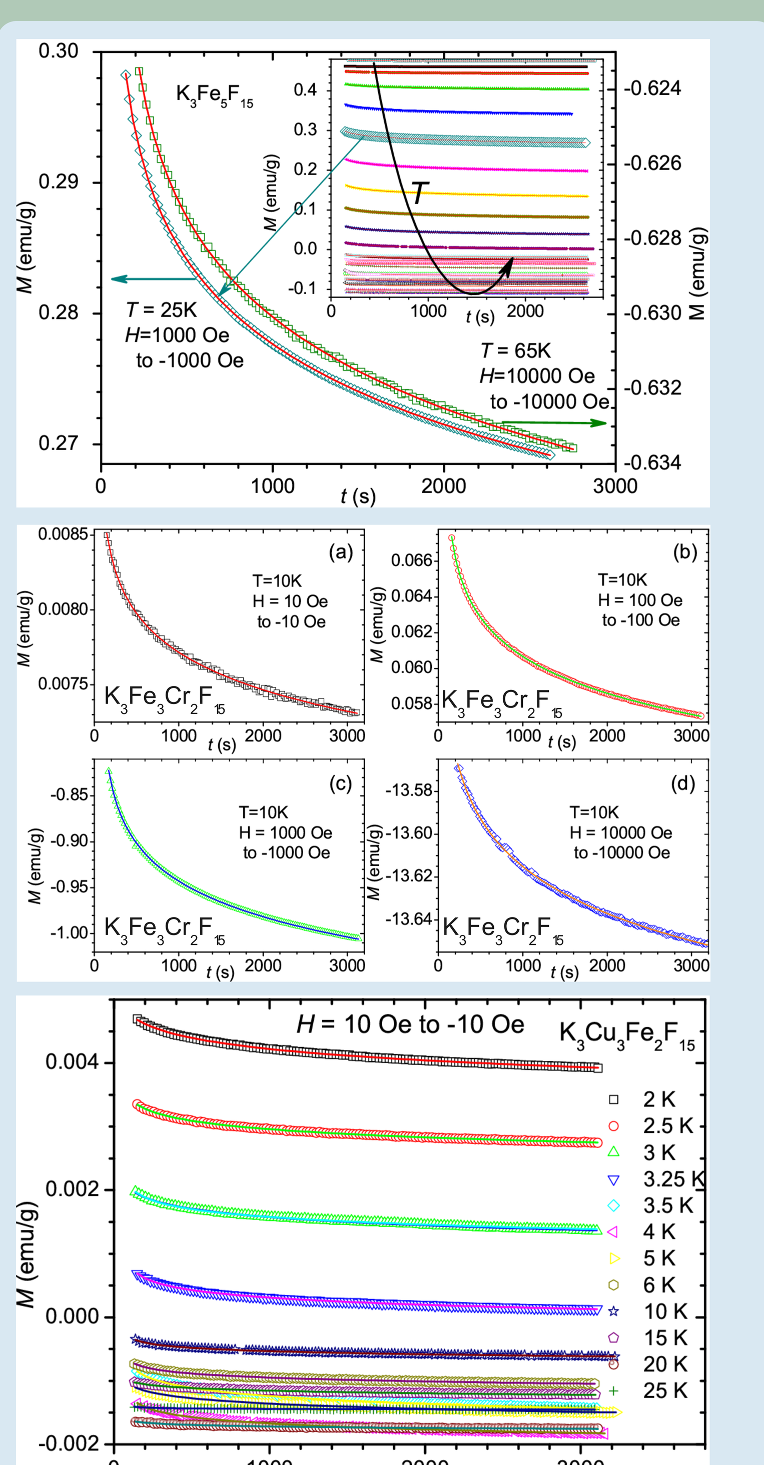


Magnetic hysteresis M(H) loops at 2K for three systems.

Splitting between the zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ curves points to the blocking/freezing of magnetic moments. For $K_3Fe_5F_{15}$ the splitting temperature (122K) does not move with change of magnetic field and it was designated as a weak ferromagnetic transition temperature [7]. In $K_3Fe_3Cr_2F_{15}$ the behaviour of ZFC-FC splitting with the change of field is in accordance to the envisaged magnetic glass-like transition [8]. Maximum at ZFC curve around 17K indicates excitation of some magnetic component of short range order, possibly the blocked superparamagnetic clusters, whose magnetic moments are activated with the increase of temperature, whereas in higher magnetic field they are not observable because of immediate turning over of the moments. In $K_3Cu_3Fe_2F_{15}$ the low field ZFC-FC splitting survives up to considerably high temperatures, whereas the increase of field moves the splitting only to the very low temperature region. This points to the existence of at least two magnetic components, possibly in accordance to the predicted nano-regions with and without magnetic order [9].

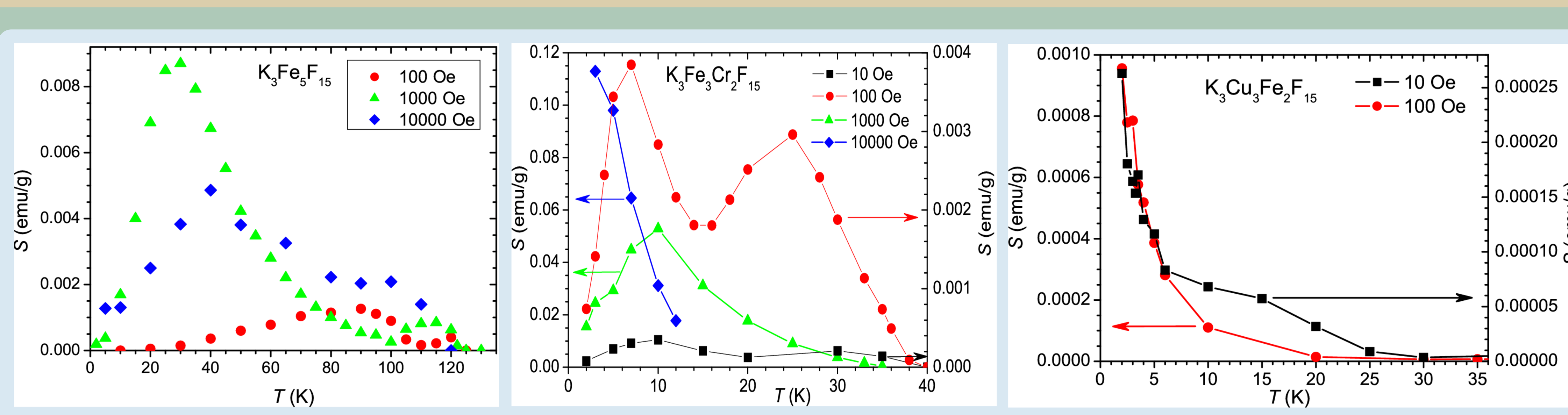
Magnetic hysteresis below transition temperature originates from the blocking of magnetic moments. With the increase of the temperature the loops become more and more narrow because lower field is needed to turn the magnetic moments over the barriers.
Completely different *M-H* characteristics between the studied compounds open the possibility to tune the coercivity, magnetization, remanence, and the nature of ordered magnetic units.

Magnetic relaxation



Relaxation of magnetization after the change of magnetic field for all three systems is observable across the quite unusually broad range of the magnetic fields and temperatures. Moreover, it is everywhere excellently fitted by logarithmic time relaxation $M(t)=M_0 - S\ln(t-t_0)$ represented by the lines.

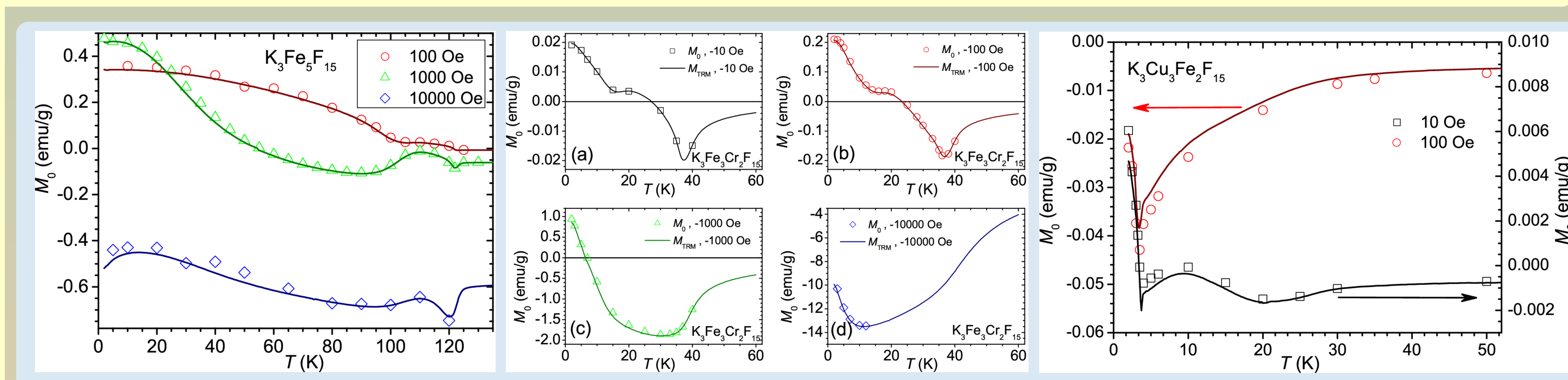
The logarithmic relaxation is characteristic of the systems where the distribution of the activation energies is present. As the system is relaxing it comes to higher and higher barriers which should be crossed over. In our systems the relaxing units of the ensemble are magnetic moments of groups/clusters of the spins.



Temperature dependence of the logarithmic relaxation rates S in different magnetic fields for $K_3M^{I}_{3}M^{II}_{2}F_{15}$ system. The lines are eye-guides.

Logarithmic relaxation rates vs. temperature for smaller fields exhibit two maxima. This means that two groups of magnetic moments contribute mostly to the relaxation of magnetization. The increase of magnetic field moves the maxima positions toward the lower temperature because in higher field the magnetic moments need smaller thermal energy to cross over the barriers. Further increase of the field leads to the extinction of one maximum because the group of moments with lower energy is turned over completely and does not contribute to the relaxation.
This model consistently explains the ZFC-FC curves, where also two regimes are observed, either via two maxima or via inflection features, showing the activation of two groups of moments at different temperatures for smaller fields and only one group for higher fields, respectively.

Excellent matching of the fitting parameter M_0 and measured thermo-remanent magnetization after the change of magnetic field further confirms the validity of dynamic model of magnetic behaviour after the change of magnetic field and the existence of two groups of moments blocked with different energy barriers.



Temperature dependence of starting magnetization M_0 in different magnetic fields for $K_3M^{I}_{3}M^{II}_{2}F_{15}$ system. Lines are the thermoremanent magnetization curves measured during the heating after the change of magnetic field.

Conclusions:

- ✗ ZFC-FC magnetization curves and magnetic hysteresis loops point to the diverse magnetic moment blocking/freezing phenomena through the $K_3M^{I}_{3}M^{II}_{2}F_{15}$ system.
- ✗ The logarithmic time relaxation of magnetization in the quite unusually broad range of temperatures and fields points to the broad distribution of magnetic moments over the blocking/freezing energies.
- ✗ All of performed experiments point to the existence of two groups of moments.
- ✗ Excellent agreement between ZFC-FC $M(T)$ curves, logarithmic relaxation rate S and starting magnetization M_0 confirm the validity of model of thermal activation of magnetic moments leading to the magnetic relaxation dynamics.
- ✗ Completely different magnetic characteristics between these compounds indicate wide tuning possibilities, that is desirable in the design of novel multiferroic materials.

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