Contribution ID: **79** Type: **poster presentation**

Magnetocaloric effect and relaxation of Mn12 molecular nanomagnet incorporated into mesoporous silica: comparative study

Tuesday, July 7, 2015 8:30 PM (1h 30m)

One of the possible applications of magnetic molecular clusters is using them for magnetic refrigeration in the low and ultra-low temperature range. Due to the high spin values <i>S</i> shown by some molecules, the total molar magnetic entropy <i>S</i>_{max}=<i>R</i>ln(2<i>S</i>+1) (<i>R</i> is a gas constant) is large and the isothermal entropy change Δ<i>S</i> on the change of applied magnetic field Δ<i>H</i> should be substantial. Values of Δ<i>S</i> or of Δ<i>T</i>_{ad} (the related adiabatic change of temperature) are the two measures of the magnetocaloric effect (MCE). It is known that magnetic anisotropy (if present) of high-spin molecules leads to strong increase of relaxation time and irreversible behaviour below the blocking temperature <i>T</i>_b. While for <i>T</i>»<i>T</i>_b molecular nanomagnets behave like superparamagnets, at <i>T</i>«<i>T</i>_b they show magnetic hysteresis resulting from slow response of the collection of isolated molecules. As has been discussed in [1], increase of magnetic anisotropy of an isolated cluster shifts the MCE maximum to higher temperatures and results in lower peak value. Another interesting feature of MCE is large Δ<i>S</i> around <i>T</i>_b and shift of the entropy variation and cooling temperature with the sweeping rate, as determined for the representative molecular cluster Mn12 [2].
Application of molecular clusters in any device needs organization of the species on a determined surface or in a particular matrix. Mesoporous silica is a stable and chemically inert material, suitable for incorporation of molecules inside the pores of nanometer size. It was found that magnetic properties of molecular clusters of the Mn12 family inserted into hexagonal SBA-15 [3, 4] or MCM-41 [5] silicas stayed globally unmodified. The present work is devoted to study the MCE and relaxation of Mn12 molecules ([Mn₁₂O₁₂(CH₃COO
immobilized in the SBA-15 mesoporous silica. In order to further improve incorporation and homogeneity of distribution the molecules inside the pores, the three stage synthesis [6] of the SBA-Mn12 samples has been adopted: (i) preparation of SBA-15 containing cyanopropyl groups (ii) hydrolysis into SBA-15 containing carboxylic acid propyl groups and (iii) functionalization of COOH groups with Mn12 molecules [7]. The similar procedure was successfully applied to obtain SBA-15 functionalized by nickel-phosphonic units. Efficiency of the syntheses and distribution of molecules inside the matrix were examined by means of X-ray diffraction, infrared spectroscopy, nitrogen sorption and magnetic measurements. The average pore diameter was 4.95 nm and the specific surface area 724 m²/g. In order to compare magnetic properties of Mn12 inserted into silica to the free molcules' behaviour, beside the SBA-Mn12 sample, the polycrystalline (Mn12_cr), as well as fine powder (Mn12_fp) samples of Mn12 were investigated.
Measurements of AC and DC magnetization were performed at the MPMS magnetometer in the temperature range 2-300 K. The activation energy <i>E</i>_a and the pre-exponential factor τ₀ determined from the Arrhenius formula for the relaxation time (τ=τ₀exp(<i>E</i>_a/<i>k</i>_B<i>T<
) are 70 K and 6.3×10⁻⁸ s for SBA-Mn12, while 68.1 K and 1×10⁻⁷ s for Mn12_cr and 67.7 K and 1×10⁻⁷ s for Mn12_fp. There is the significant difference in the distribution of the relaxation times: at T = 5 K α=0.24 for SBA-Mn12, while 0.11 and 0.13 for Mn12_cr and Mn12_fp respectively. Temperature dependence of the low field magnetization for all samples reveals bifurcation of the FC and ZFC branches below <i>T</i>_b=3.4 K, which is a sign of the irreversible state and non-zero remanent magnetization <i>M</i>_R. Magnetocaloric effect was determined from the isothermal demagnetization curves, measured under decreasing field from 5 T to 0 T at small temperature intervals in the range from 2 K to 20 K. The isothermal entropy change |Δ<i>S</i>| for all samples shows a narrow maximum below <i>T</i>_b and then slowly decreases or levels off. For SBA-Mn12, |Δ<i>S</i>|^{max}=13.8 J mol⁻¹ K⁻¹ at <i>T</i>=2.8 K and is smaller than

that for Mn12_cr (15.4 J mol⁻¹ K⁻¹ at 3.2 K) and for Mn12_fp (15 J mol⁻¹ K⁻¹ at 3.2 K). The narrow peak of MCE is the result of small sweeping rate of applied magnetic field (3×10⁻⁴ Hz) in the experiment. In order to understand better the mechanism of the irreversible magnetic entropy change we measured also magnetization curves on field increasing. The different appearance of that result will be discussed.

[1] M. Evangelisti and E. K. Brechin, <i>Dalton Trans.</i> 39 (2010) 4672.
[2] F. Torres, J. M. Hernandez, X. Bohigas, and J Tejada, <i>Appl. Phys. Lett.</i> 77 (2000) 3248.
[3] T. Coradin, J. Larionova, A. A. Smith, G. Rogez, R. Clerac, Ch. Guerin, G. Blondin, R. E. P. Winpenny, C. Sanchez, and T. Mallah, <i>Adv. Mater.</i> 14 (2002) 896.
[4] S. Willemin, G. Arrachart, L. Lecren, J. Larionova, T. Coradin, R. Clerac, T. Mallah, Ch. Guerin, and C. Sanchez, <i>New J. Chem.</i> 27 (2003) 1533.
[5] M. Clemente-Leon, E. Coronado, A. Forment-Aliaga, P. Amoroz, J. Ramirez-Castellanos, J. M. Gonzalez-Calbet, <i>J. Mater. Chem.</i> 13 (2003) 3089.
[6] B. Folch, J. Larionova, Y. Guari, C. Guerin, A. Mehdi. and C. Reye, <i>J. Mater. Chem.</i> 14 (2004) 2703.
[7] Ł. Laskowski, M. Laskowska, M. Bałanda, M. Fitta, J. Kwiatkowska, K. Dziliński, A. Karczmarska, <i>Micropor. Mesopor. Mat.</i> 200 (2014) 253-259.

Primary author: Prof. BAŁANDA, Maria (Institute of Nuclear Physics PAN, Kraków)

Co-authors: Dr FITTA, Magdalena (Institute of Nuclear Physics PAN, Kraków); Ms LASKOWSKA, Magdalena (Institute of Intelligent Computational Systems, Częstochowa University of Technology, Poland); Mr GAJEWSKI, Marcin (Institute of Nuclear Physics PAN, Kraków); Dr PEŁKA, Robert (Institute of Nuclear Physics PAN, Kraków); Dr LASKOWSKI, Łukasz (Institute of Intelligent Computational Systems, Częstochowa University of Technology, Poland)

Presenter: Prof. BAŁANDA, Maria (Institute of Nuclear Physics PAN, Kraków)

Session Classification: Posters

Track Classification: molecular magnets and nanomagnets