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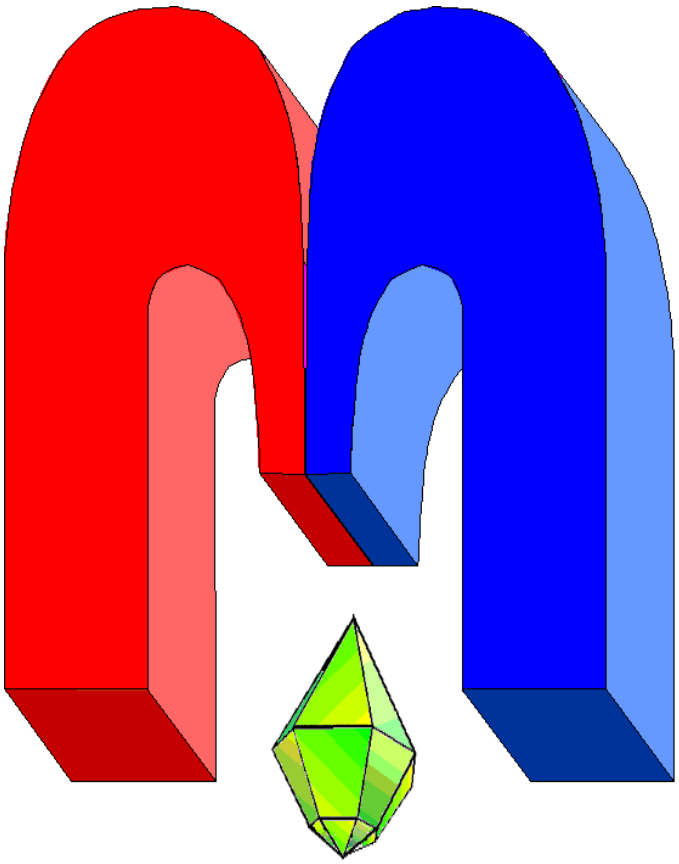

# Magnetic Resonance in Solids

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# Magnetic properties of $DyF_3$ micro- and nanoparticles

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The AC/DC magnetic susceptibility and heat capacity of microsized and nanosized $DyF_3$ particles were measured. These measurements were used to estimate the influence of the size of $DyF_3$ particles on their magnetic properties. Dipolar ferromagnetic transition was observed in susceptibility measurements for $DyF_3$ microparticles at $T_C = 2.54$ K, whereas $DyF_3$ nanosized particles remain paramagnetic down to the lowest achieved temperature of 1.8 K. This peculiar behaviour might indicate the change of magnetic properties due to crossover from macro to nanoscale physics.

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**Keywords**: magnetization, heat capacity, Curie temperature, $DyF_3$

## 1. Introduction

Lanthanide fluoride $ReF_3$ (Re = rare earth) nanoparticles have been used in many fields of science and technology, e.g. as active medium in solid state lasers, biological labels, waveguide devices, optical-display phosphors [1-8]. The lanthanide ions (La-Lu) containing compounds and materials are perspective in use as magnetic resonance contrast agents at low and high magnetic fields [9-10]. The microwave-assisted synthesis method was successfully used for preparation, structure and size modification of $PrF_3$ and $DyF_3$ nanoparticles [11-20].

There are articles devoted to $DyF_3$ nanoparticles synthesis [20-23]. The $DyF_3$ nanoparticles are used for Nd-Fe-B magnets fabrication and for other applications [24-28]. The $DyF_3$ compound is a dipolar ferromagnet with a phase transition temperature $T_C = 2.55$ K [29]. At the same time magnetic transition to ferromagnetic state is not observed in $TbF_3$ nanoparticles so far [10]. In this sense, the dependence of the phase transition temperature as a function of a particle size itself is one of the intriguing problem.

It is also known that magnetic properties of nanoparticles are related to the size of the particles. The reduction of Curie temperature with decrease particles size was observed [30-32]. Finite-size effect is related to the increase of surface to volume ratio with decreasing of nanoparticles size, because the surface properties are different from the bulk material [33].

In this paper magnetic properties study by magnetometry and heat capacity measurements are reported.

## 2. Materials and methods

A crystalline microsized powder $DyF_3$ was used as sample #1. The powder was prepared from a $DyF_3$ single crystal grown at the Research Laboratory of Magnetic Radiospectroscopy and Quantum Electronics of Kazan Federal University by mechanical grinding in a sapphire mortar. Then the powder was sifted with a 45 μm sieve. Typical size of particles was 1-45 μm.

The $DyF_3$ nanoparticles with average particle size of about 16-18 nm (sample #2) were synthesized by the 7 hour microwave-assisted colloidal hydrothermal method described in [21].

The crystal structure of all samples was characterized by X-ray diffraction (XRD). Powder X-ray diffraction experiments were done on Bruker D8 Advance X-ray diffractometer with use of copper $K\alpha$ ($\alpha = 1.5418$ Å) radiation and continuous scan. Scan speed 0.005° per second in the range of diffraction angles 20°-60° was chosen.

Experimental XRD patterns of samples are shown in fig. 1. The PowderCell software [34] allows to simulate the diffraction pattern of $DyF_3$. The XRD patterns can be indexed to a pure orthorhombic phase $DyF_3$ (space group *Pnma* ($D_{2h}^{16}$)) with lattice constant $a = 6.460$ Å, $b = 6.9060$ Å and $c = 4.3760$ Å [35]. In the measured X-ray diffraction spectrum of the $DyF_3$ micropowder no any extra peaks were observed (fig. 1a). The X-ray diffraction measurements in the $DyF_3$ nanopowder reveal the presence of two very weak diffraction maximums ($2\theta \approx 21.790°$ and $2\theta \approx 26.610°$) that do not belong to $DyF_3$ structure. Thus, in the nanopowder there is only a small admixture of the unknown crystalline phase.

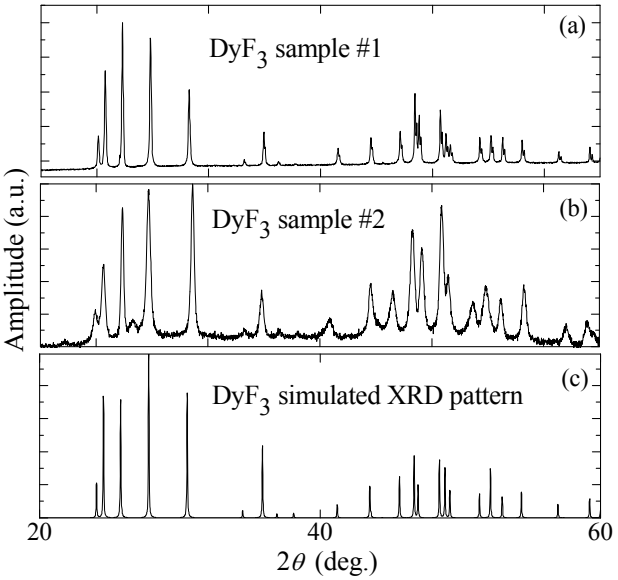


**Figure 1.** (a, b) The experimental XRD patterns of $DyF_3$ samples #1 and #2. (c) The simulated $DyF_3$ XRD patterns using PowderCell software.

The magnetic properties of micro and nanosized $DyF_3$ particles were investigated by static (DC) and dynamic (AC) magnetic susceptibility measurements using a Magnetic Property Measurement System XL-7 by Quantum Design. All performed static susceptibility experiments were done in zero-field cooled regime in the temperature range of 1.8-300 K. The external magnetic field $H_{DC}$ = 100 Oe was applied during heating up of the sample in all measurements. For acquiring the AC susceptibility data the driving field 5 Oe ($H_{AC}$) was applied and the frequency was varied in the range of 5-500 Hz. For sample #1 the dynamic susceptibility measurements were performed at $H_{DC}$ = 100 Oe, whereas measurements of the sample #2 were performed in the absence of external magnetic field ($H_{DC}$ = 0 Oe).

The temperature dependence of the static magnetic susceptibility of $DyF_3$ micropowder (samples #1 and #2) is shown in fig. 2. The static susceptibility is described by Curie-Weiss law $\chi = C/(T - T_C)$, where $C$ is Curie constant, $T$ is the absolute temperature and $T_C$ is the Curie temperature, corresponding to the ferromagnetic transition. At high temperatures the both susceptibilities of the samples show paramagnetic behaviour, while at low temperatures $\chi(T)$ curves for micro- and nano-samples exhibit different features.

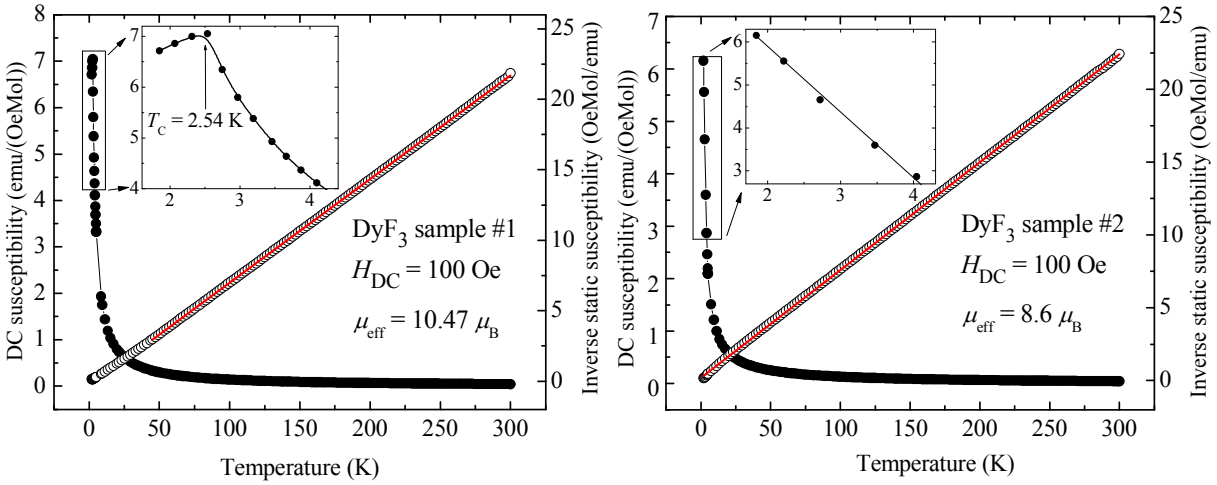


**Figure 2.** The temperature dependencies of DC magnetic susceptibility (●) and inverse static susceptibility (○) of $DyF_3$ (samples #1 and #2) in external magnetic field of 100 Oe. The black line shows an eye guide for susceptibility data. The red solid line represents the fit to Curie-Weiss law for inverse static susceptibility data. The inset represents DC susceptibility data near $T_C$.

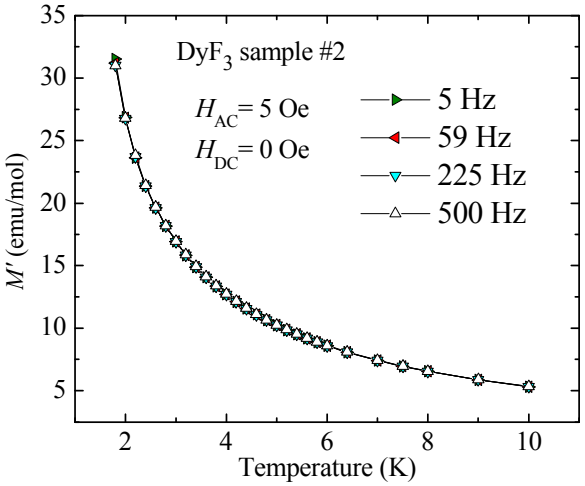


**Figure 3.** The real part of the magnetization versus temperature measured at 5 Oe for $DyF_3$ nanoparticles (sample #2).

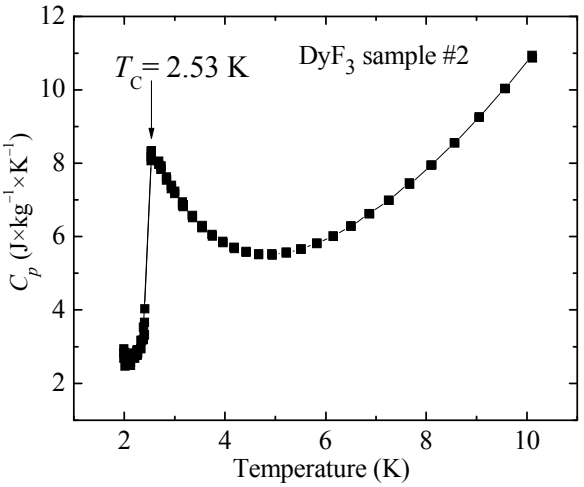


**Figure 4.** The temperature dependence of the specific heat of $DyF_3$ nanoparticles (sample #2).

The magnetic transitions of microsized particles were observed at $T_C = 2.54$ K, which is in a good agreement with the Curie temperature reported for $DyF_3$ single crystal [29]. In contrast to this result for $DyF_3$ nanoparticles evidences of the magnetic transition were not observed to the lowest achieved temperature 1.8 K.

For the further analysis we plot inverse static susceptibility $\chi^{-1}$ as a function of temperature (see fig. 2). For micro powdered $DyF_3$ inverse static susceptibility $\chi^{-1}$ holds linear temperature dependence down to $T \approx 50$ K and slightly deviates from linearity below this temperature. For nanosized particles the $\chi^{-1}(T)$ shows pure paramagnetic-like behaviour in whole temperature range. From the linear fit of the high-temperature part (above 50 K) of $\chi^{-1}$ the Curie constants were obtained and effective magnetic moments were evaluated, which are 10.47 $\mu_B$ and 8.6 $\mu_B$ per magnetic ion for micropowder and nanopowder, correspondingly.

The dynamic magnetic susceptibility measurements are also a powerful and sensitive tool to study magnetic phase transitions, such as ferromagnetic transitions. The AC measurement provides an accurate determination of the magnetic ordering temperature $T_C$ [36]. In fig. 3 the temperature dependence of real part of magnetization $M'$ for $DyF_3$ nanoparticles (sample #2) is presented. As it can be seen from fig. 3 there is no sign of magnetic phase transitions in the whole temperature range.

The heat capacity of the samples measured using Physical Properties Measurement System (PPMS) from Quantum Design. The temperature dependency of the specific heat $C_p$ of $DyF_3$ nanosized sample is shown in fig. 4.

The data of the specific heat measurements shows an anomaly with the peak at $T_C = 2.53$ K for nanosized sample #2 corresponding to the magnetic phase transition of $DyF_3$ single crystal. The specific heat anomaly in $DyF_3$ is in a good agreement with the specific heat measurements reported for $DyF_3$ [37].

At the first sight, comparison of heat capacity and magnetization data might look puzzling: the dipolar ferromagnetic transition is observed for both micro and nano sized particles as a kink in the specific heat at $T = 2.53$ K, but there is no sign of magnetic phase transition for nanoparticles in the static and dynamic susceptibility measurements.

The phase transition was not observed by the magnetization measurements, possibly due to the influence of surface effects and strong disordering of crystalline fields. Another possible explanation is the superparamagnetism phenomena. When the size of particles is sufficiently small, a single domain state become preferable. The direction of magnetic moment of such particle may change due to thermal fluctuations and in the absence of magnetic field the averaged magnetization is zero. In this state the external magnetic field polarize magnetization of nanoparticles. The temperature behaviour

of the static susceptibility of superparamagnet nanoparticles is similar to a paramagnet even at temperatures below $T_C$. Therefore, it is very likely that ferromagnetic transition takes place in each single nanoparticle at $T_C = 2.53$ K as it was shown by heat capacity measurements but for assemble of such nanoparticles still show paramagnetic behaviour. For a more detailed study it is necessary to prepare a series of nanoparticle samples in the broad range of size. NMR experiments will also be carried out to study the static and fluctuating magnetic fields of the solid matrix at low temperatures using liquid $^3$He as a probe.

## 3. Conclusions

The AC/DC magnetic susceptibility and heat capacity of microsized and nanosized $DyF_3$ particles were measured. Dipolar ferromagnetic transition was observed in susceptibility measurements for $DyF_3$ microparticles at $T_C = 2.54$ K, whereas nanosized $DyF_3$ particles remain paramagnetic-like down to the lowest achieved temperature 1.8 K. Specific heat measurements show an anomaly with a peak at $T_C = 2.53$ K for nanosized $DyF_3$. This peculiar behavior might indicate the change of magnetic properties due to crossover from the bulk (micrometer) to nanoscale physics.

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## References

1. Chatterjee D.K., Rufaihah A.J., Zhang Y. *Biomaterials* **29**, 937 (2008)
2. Wang F., Liu X., *Chem. Soc. Rev.* **38**, 976 (2009)
3. Kong D.Y., Wang Z.L., Lin C.K., Quan Z.W., Li Y.Y., Li C.X. Lin J., *Nanotechnology* **18**, 075601 (2007)
4. Wang F., Zhang Y., Fan X., Wang M. *Nanotechnology* **17**, 1527 (2006)
5. Ansari A.A., Singh N., Singh S.P. *J. Nanopart. Res.* **10**, 703 (2008)
6. Dekker R., Klunder D.J.W., Borreman A., Diemeer M.B.J., Wörhoff K., Driessen A., Stouwdam J.W., Van Veggel F.C.J.M. *Appl. Phys. Lett.* **85**, 6104 (2004)
7. Jüstel T., Nikol H., Ronda C. *Angew. Chem. Int. Ed.* **37**, 3084 (1998)
8. Pudovkin M.S., Morozov O.A., Pavlov V.V., Korableva S.L., Lukinova E.V., Osin Y.N., Evtugyn V.G., Safiullin R.A., Semashko V.V. *J. Nanomater.* **2017**, 3108586 (2017)
9. Norek M., Peters J.A. *Prog. Nucl. Magn. Reson. Spectrosc.* **59**, 64 (2011)
10. Zheng X., Wang Y., Sun L., Chen N., Li L., Shi S., Malaisamy S., Yan C. *Nano Res.* **9**, 1135 (2016)
11. Ma L., Chen W.-X., Zheng Y.-F., Zhao J., Xu Z. *Mater. Lett.* **61**, 2765 (2007)
12. Tagirov M.S., Alakshin E.M., Gazizulin R.R., Egorov A.V., Klochkov A.V., Korableva S.L., Kuzmin V.V., Nizamutdinov A.S, Kono K., Nakao A., Gubaidullin A.T. *J. Low Temp. Phys.* **162**, 645 (2011)
13. Alakshin E.M., Gabidullin B.M., Gubaidullin A.T., Klochkov A.V., Korableva S.L., Neklyudova M.A., Sabitova A.M., Tagirov M.S. *arXiv:1104.0208* (2011)
14. Alakshin E.M., Aleksandrov A.S., Egorov A.V., Klochkov A.V., Korableva S.L., Tagirov M.S. *JETP Lett*. **94**, 240 (2011)
15. Alakshin E.M., Blokhin D.S., Sabitova A.M., Klochkov A.V., Klochkov V.V., Kono K., Korableva S.L., Tagirov M.S. *JETP Letters*. **96**, 181 (2012)
16. Alakshin E.M., Gazizulin R.R., Klochkov A.V., Korableva S.L., Kuzmin V.V., Sabitova A.M.,

Safin T.R., Safiullin K.R., Tagirov M.S. *JETP Lett*. **97**, 579 (2013)

17. Pudovkin M.S., Korableva S.L., Krasheninnicova A.O., Nizamutdinov A.S., Semashko V.V., Zelenihin P.V., Alakshin E.M., Nevzorova T.A. *J. Phys.: Conf. Ser.* **560**, 012011 (2014)
18. Alakshin E.M., Gazizulin R.R., Klochkov A.V., Korableva S.L., Safin T.R., Safiullin K.R., Tagirov M.S. *Opt. Spectrosc.* **116**, 721 (2014)
19. Gazizulina A.M., Alakshin E.M., Baibekov E.I., Gazizulin R.R., Zaharov M.Yu., Klochkov A.V., Korableva S.L., Tagirov M.S. *JETP Lett*. **99**, 149 (2014)
20. Ye X., Chen J., Engel M., Millan J.A., Li W., Qi L., Xing G., Collins J.E., Kagan C.R., Li J., Glotzer S.C., Murray C.B. *Nat. Chem.* **5**, 466 (2013)
21. Alakshin E.M., Klochkov A.V., Kondratyeva E.I., Korableva S.L., Kiiamov A.G., Nuzhina D.S., Stanislavovas A.A., Tagirov M.S., Zakharov M.Yu., Kodjikian S. *J. Nanomater.* **2016**, 7148307 (2016)
22. Bhowmik S., Goraia T., Maitra U. *J. Mater. Chem. C* **2**, 1597 (2014)
23. Li C., Yang J., Yang P., Lian H., Lin J. *Chem. Mater.* **20**, 4317 (2008)
24. Park S.-E., Kim T.-H., Lee S.-R., Namkung S., Jang T.S. *J. Appl. Phys*. **111**, 07A707 (2012)
25. Cao X.J., Chen L., Guo S., Li X.B., Yi P.P., Yan A.R., Yan G.L. *J. Alloys Compd*. **63**, 315 (2015)
26. Sawatzki S., Dirba I., Schultz L., Gutfleisch O. *J. Appl. Phys*. **114**, 133902 (2013)
27. Sueptitz R., Sawatzki S., Moore M., Uhlemann M. *Mater. Corros.* **66**, 152 (2015)
28. Chen D., Yu Y., Huang P., Wang Y. *CrystEngComm* **11**, 1686 (2009)
29. Savinkov A.V., Korableva S.L., Rodionov A.A., Kurkin I.N., Malkin B.Z., Tagirov M.S., Suzuki H., Matsumoto K., Abe S. *J. Phys.: Condens. Matter* **20**, 485220 (2008)
30. Chang Y.Q., Xu X.Y., Luo X.H., Chen C.P., Yu D.P. *J. Cryst. Growth* **264**, 232 (2004)
31. Rong C., Li D., Nandwana V., Poudyal N., Ding Y., Wang Z.L., Zeng H., Liu J.P. *Adv. Mater.* **18**, 2984 (2006)
32. Alloyeau D., Ricolleau C., Mottet C., Oikawa T., Langlois C., Bouar Y.Le., Braidy N., Loiseau A. *Nat. Mater.* **8**, 940 (2009)
33. Sun L., Searson P.C., Chien C.L. *Phys. Rev. B* **61**, R6463 (2000)
34. Kraus W., Nolze G. *J. Appl. Crystallogr.* **29**, 301 (1996)
35. Zalkin A., Templeton D.H. *J. Am. Chem. Soc.* **75**, 2453 (1953)
36. Balanda M. *Acta Phys. Pol. A* **124**, 964 (2013)
37. Holmes L.M., Hulliger F., Guggenheim H.J., Maita J.P. *Phys. Lett. A* **50**, 163 (1974)