Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2022, 32, 305–307

Mendeleev Communications

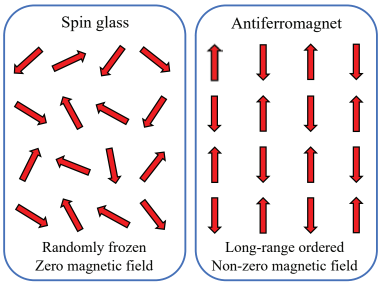
Spin-glass-like behavior in $SmFeAsO_{0.8}F_{0.2}$

Nikolai D. Zhigadlo*[a] and Roman Puzniak[b]

[a] CrystMat Company, CH-8037 Zurich, Switzerland. E-mail: nzhigadlo@gmail.com
[b] Institute of Physics, Polish Academy of Sciences, PL-02668 Warsaw, Poland

DOI: 10.1016/j.mencom.2022.05.004

The iron-based oxypnictide superconductor $SmFeAsO_{0.8}F_{0.2}$ was synthesized under high pressure and investigated by measuring the dc magnetic susceptibility. The zero-field cooled (ZFC) magnetic susceptibility confirmed the bulk superconductivity of the sample with a critical temperature $T_c \simeq 50$ K and a significant jump in magnetization at ~4.3 K, usually attributed to the antiferromagnetic ordering of Sm^{3+} ions in this system. Since the occurrence of the jump depends on the cooling history, our data strongly suggest a spin-glass-like behavior.



Keywords: oxypnictide superconductor, $SmFeAsO_{0.8}F_{0.2}$, high-pressure synthesis, magnetic susceptibility, spin-glass-like behavior.

For many decades, the study of spin glasses has been an attractive topic in magnetism.[1–5] Basically, a spin glass can be defined as a set of interacting magnetic moments originating from spins, in which the interactions are randomly distributed in sign and possibly in magnitude.[5] The many available arrangements of spins with comparable energies produce a huge number of metastable states. Hence, finding the absolute minimum is extremely difficult, and a spin glass is always out of equilibrium. The first spin glass materials discovered were nonmagnetic metals (Au, As, Pt, *etc.*), in which a few percent of magnetic atoms (Fe, Mn, *etc.*) were randomly dispersed.[6] At present, many different systems are known to exhibit spin-glass or spin-glass-like behavior; among them are metals including superconductors, metallic glasses, dilute magnetic alloys, semimetals and insulating glasses. All these materials exhibit particular dynamics of magnetization, and many interesting effects are observed in magnetic susceptibility.[5]

The discovery of Fe-based high-temperature superconducting materials has opened a new window into the physics of unconventional superconductors. Many of these materials contain at least two magnetic elements (Fe and a magnetic rare-earth metal). Spin-glass behavior due to spin disorder and magnetic frustration below a certain freezing temperature has been reported in Fe-based superconductors such as P-doped $EuFe_2As_2$,[7] Co-doped $BaFe_2As_2$,[8] Se-doped FeTe[9] and Ce-doped $CaFe_2As_2$.[10] The parent compound SmFeAsO is one of the members of a large family of LnFeAsO (Ln1111, Ln = lanthanide) exhibiting two types of magnetic orders: antiferromagnetic (AFM) ordering of Fe spins in the *ab* plane at ~130 K and ordering of Sm spins along the *c* axis at ~5 K (Figure 1).[11,12] The AFM ordering of the Fe spins can be suppressed upon appropriate doping; hence, superconductivity emerges at the expense of antiferromagnetism, whereas the Sm ordering survives.[13,14] Interestingly, the Nd moments also align in the *c* direction in NdFeAsO compounds with the same AFM alignment as in SmFeAsO, *i.e.* low-temperature magnetism in these compounds may share a similar underlying physics.[15] Despite extensive experimental efforts over the past years, the interplay between superconductivity and magnetism in the LnFeAsO family remains an important open issue, which requires further exploration.

When studying the $SmFeAsO_{0.8}F_{0.2}$ superconductor by measuring the standard dc magnetic susceptibility using both zero-filed-cooling (ZFC) and field-cooling (FC) protocols, we observed a significant jump in magnetization at ~4.3 K. Such a jump was interpreted as a result of the antiferromagnetic ordering of Sm^{3+} ions in this system,[16] which mimics electron-doped high-T_c cuprate $Sm_{2-x}Ce_xCuO_{4-\delta}$.[17] In our opinion, the situation is somewhat more complicated if we take into account that the appearance of the magnetization jump depends on the cooling history of the sample. The present data suggest a spin-glass-like behavior of $SmFeAsO_{0.8}F_{0.2}$ in the low-temperature region.

A polycrystalline sample with nominal composition $SmFeAsO_{0.8}F_{0.2}$ was prepared by heating a stoichiometric mixture of high-purity SmAs, FeAs, Fe_2O_3, Fe and SmF_3 powders in a boron nitride crucible at a temperature of 1350 °C and a pressure of 3 GPa for 4.5 h (for details, see Online Supplementary Materials and previously published works[18–20]). X-ray measurements revealed a high homogeneity and single-phase

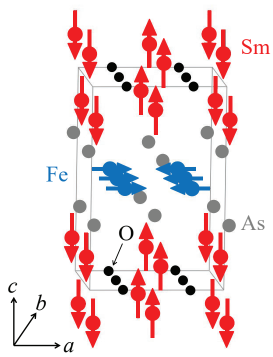


Figure 1 Magnetic structures adopted by the Fe and Sm sublattices in SmFeAsO below 5 K (two unit cells are shown).

crystalline nature of the sample, as well as the absence of any significant amounts of impurities. The stoichiometry of the resulting sample was revealed by energy-dispersive X-ray spectroscopy analysis and further confirmed by X-ray structure refinement (for details, see Online Supplementary Materials). The temperature dependence of the magnetic susceptibility of the powdered polycrystalline $SmFeAsO_{0.8}F_{0.2}$ sample was measured in an external magnetic field of 10 Oe using both ZFC and FC protocols (for details, see Online Supplementary Materials). To eliminate the possible influence of non-uniformities in the device magnet on the measurement results, especially at very low fields, efforts were made to minimize the remnant field.

Figure 2(*a*) shows the characteristic change in magnetization as a function of temperature. The sample was cooled in a zero field from the temperature region of the paramagnetic state to a temperature of 1.8 K. After reaching the desired temperature and waiting for 1 h, the evolution of magnetization was measured under a tiny applied magnetic field of 10 Oe. The measurement revealed the bulk nature of superconductivity with a critical temperature $T_c \simeq 50$ K. The reduced low-temperature diamagnetic response, equal to ~27% of the ideal superconductivity response, is due to the relatively small grain size of the material under study, comparable to its penetration depth. The low-temperature part of the ZFC curve is shown in Figure 2(*b*), where a small but distinct jump in magnetization is observed at ~4.3 K (curve *1*).

In the published data, this transition is usually assigned to the AFM ordering of the Sm^{3+} ions in this system.[16,21] However, the present data suggest rather a spin-glass-like behavior, since the appearance of the jump depends on the cooling history of the sample. It turned out that the magnetization jump can be removed by heating the $SmFeAsO_{0.8}F_{0.2}$ sample above the jump temperature and cooling it again. This is illustrated in Figure 2(*b*), which shows the results of measurements carried out in a magnetic field of 10 Oe upon heating after zero-field cooling (curve *1*), then upon cooling in a field (curve *2*) and further upon reheating in a field (curve *3*). This behavior suggests a large degree of disorder in the Sm^{3+} magnetic moments and confirms the coexistence of spin-glass-like ordering and superconductivity in $SmFeAsO_{0.8}F_{0.2}$. At high temperatures, the Sm subsystem is in the paramagnetic phase and all spins fluctuate. In our case, the ZFC curve [Figure 2(*b*), curve *1*] indicates a nonequilibrium state in the frozen phase, since the field was applied at a low temperature. When the sample is cooled to low temperatures in the absence of an external field, many competing metastable states appear, separated by high-energy barriers, and the system can be tracked in any of them. By contrast, if the material is cooled in a non-zero external field, *i.e.*, in the FC mode [Figure 2(*b*), curve *2*], the magnetization can be considered as equilibrium in the first approximation, and the Sm^{3+} spins align with the magnetic field, which leads to the antiferromagnetic order.

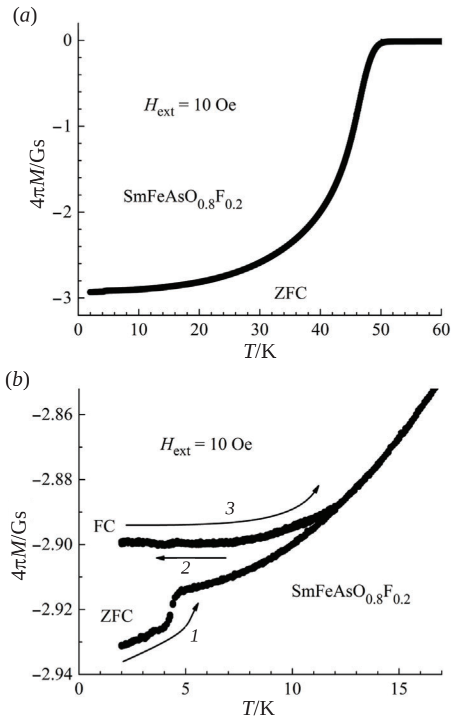


Figure 2 Temperature dependence of the magnetization of $SmFeAsO_{0.8}F_{0.2}$ recorded using the standard ZFC and FC protocols. (*a*) The sample was first cooled in a zero field to 1.8 K, and measurements were carried out while heating it after applying an external field of 10 Oe. (*b*) Measurements were performed in a magnetic field of 10 Oe (*1*) upon heating after ZFC, (*2*) then upon cooling in the field and (*3*) further upon reheating in the field. A small but distinct jump in magnetization occurs at ~4.3 K. The onset of irreversibility occurs at ~12 K, where the ZFC and FC curves diverge.

In our case, the spin-glass-like feature is rather weak, and its possible origin can be ascribed to (i) random magnetic exchange interactions between inhomogeneously distributed Sm^{3+} spins, (ii) magnetic exchange coupling between Fe and Sm spins, which leads to frustration among the Sm spins, or to both. The latter case was actually observed in parent single crystalline SmFeAsO.[11] An X-ray resonant magnetic scattering experiment showed that due to the interconnection between Fe and Sm, the induced moments of Sm or the coupled moments of Fe and Sm appear at a temperature much higher than the magnetic ordering temperature of Sm, $T_{Sm} \simeq 4.3$ K. A similar interplay between two magnetic sublattices was also observed in the NdFeAsO system.[22] Such coupling, however, can be ruled out for $SmFeAsO_{0.8}F_{0.2}$, since F doping suppresses AFM ordering, and yet, below $T \leqslant 12$ K we can see that the ZFC and FC curves diverge [Figure 2(*b*)]. Thus, we can hypothesize that, in addition to the randomly distributed spins of Sm, the coupled moments of Fe and Sm can also contribute to the spin-glass-like behavior of $SmFeAsO_{0.8}F_{0.2}$.

It is interesting to note that the magnetic structure of the Sm subsystem in SmFeAsO and SmFeAs(O,F) is essentially the same as that adopted by the Sm moments in Sm_2CuO_4,[17] and that all compounds exhibit an unusual insensitivity of T_{Sm} to an externally applied magnetic field.[21,23] It is still unclear why and how the Sm ordering coexists with superconductivity in $SmFeAsO_{0.8}F_{0.2}$ and what role it plays in setting the high superconducting transition temperatures observed in this series.

In summary, the observed dependence of magnetization at low temperature on history provides evidence for the existence of a spin-glass-like state in superconducting $SmFeAsO_{0.8}F_{0.2}$. This system exhibits spin-glass-like features when the sample is cooled under zero-field conditions. The origin of this behavior is probably due to the inhomogeneous distribution of Sm^{3+} spins in the Sm sublattice, which is accompanied by weak interactions between the Fe and Sm spins in the Fe and Sm sublattices. Further studies are needed to identify the precise magnetic structure and understand the complex interplay between the Sm and Fe sublattices. Determining its nature is an important attempt to understand the magnetism and superconductivity of the LnFeAsO family.

The authors would like to acknowledge support from the Laboratory for Solid State Physics, ETH Zurich, where this study was initiated, and thank T. Shiroka for reading the manuscript critically and for helpful comments.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.004.

References

1 K. Binder and A. P. Young, *Rev. Mod. Phys.*, 1986, **58**, 801.
2 J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor and Francis, London, 1993.
3 *Spin Glasses and Random Fields*, ed. A. P. Young (*Series on Directions in Condensed Matter Physics*, *vol. 12*), World Scientific, Singapore, 1997.
4 J. A. Mydosh, *Rep. Prog. Phys.*, 2015, **78**, 052501.
5 E. Vincent and V. Dupuis, in *Frustrated Materials and Ferroic Glasses*, eds. T. Lookman and X. Ren, Springer, 2018, pp. 31–56.
6 V. Cannella and J. A. Mydosh, *Phys. Rev. B*, 1972, **6**, 4220.
7 S. Zapf, H. S. Jeevan, T. Ivek, F. Pfister, F. Klingert, S. Jiang, D. Wu, P. Gegenwart, R. K. Kremer and M. Dressel, *Phys. Rev. Lett.*, 2013, **110**, 237002.
8 A. P. Dioguardi, J. Crocker, A. C. Shockley, C. H. Lin, K. R. Shirer, D. M. Nisson, M. M. Lawson, N. Aproberts-Warren, P. C. Canfield, S. L. Bud'ko, S. Ran and N. J. Curro, *Phys. Rev. Lett*., 2013, **111**, 207201.
9 C. S. Yadav and P. L. Paulose, *J. Appl. Phys*., 2010, **107**, 083908.
10 K. Nadeem, W. Zhang, D. Y. Chen, Z. A. Ren and X. G. Qiu, *Sci. Rep.*, 2015, **5**, 10700.
11 S. Nandi, Y. Su, Y. Xiao, S. Price, X. F. Wang, X. H. Chen, J. Herrero-Martin, C. Mazzoli, H. C. Walker, L. Paolasini, S. Francoual, D. K. Shukla, J. Strempfer, T. Chatterji, C. M. N. Kumar, R. Mittal, H. M. Rønnow, C. Rüegg, D. F. McMorrow and T. Brückel, *Phys. Rev. B*, 2011, **84**, 054419.
12 A. Ricci, N. Poccia, B. Joseph, L. Barba, G. Arrighetti, G. Ciasca, J.-Q. Yan, R. W. McCallum, T. A. Lograsso, N. D. Zhigadlo, J. Karpinski and A. Bianconi, *Phys. Rev. B*, 2010, **82**, 144507.
13 M. R. Cimberle, F. Canepa, M. Ferretti, A. Martinelli, A. Palenzona, A. S. Siri, C. Tarantini, M. Tropeano and C. Ferdeghini, *J. Magn. Magn. Mater*., 2009, **321**, 3024.
14 D. H. Ryan, J. M. Cadogan, C. Ritter, F. Canepa, A. Palenzona and M. Putti, *Phys. Rev. B*, 2009, **80**, 220503(R).
15 M. G. Kim, J.-W. Kim, J.-Q. Yan, A. I. Goldman and A. Kreyssig, *Phys. Rev. B*, 2019, **100**, 224401.
16 L. Ding, C. He, J. K. Dong, T. Wu, R. H. Liu, X. H. Chen and S. Y. Li, *Phys. Rev. B*, 2008, **77**, 180510(R).
17 I. W. Sumarlin, S. Skanthakumar, J. W. Lynn, J. L. Peng, Z. Y. Li, W. Jiang and R. L. Greene, *Phys. Rev. Lett.*, 1992, **68**, 2228.
18 N. D. Zhigadlo, S. Katrych, Z. Bukowski, S. Weyeneth, R. Puzniak and J. Karpinski, *J. Phys.: Condens. Matter*, 2008, **20**, 342202.
19 N. D. Zhigadlo, S. Katrych, S. Weyeneth, R. Puzniak, P. J. W. Moll, Z. Bukowski, J. Karpinski, H. Keller and B. Batlogg, *Phys. Rev. B*, 2010, **82**, 064517.
20 M. Calamiotou, D. Lampakis, E. Siranidi, J. Karpinski, N. D. Zhigadlo and E. Liarokapis, *Phys. C*, 2012, **483**, 136.
21 S. Weyeneth, P. J. W. Moll, R. Puzniak, K. Ninios, F. F. Balakirev, R. D. McDonald, H. B. Chan, N. D. Zhigadlo, S. Katrych, Z. Bukowski, J. Karpinski, H. Keller, B. Batlogg and L. Balicas, *Phys. Rev. B*, 2011, **83**, 134503.
22 W. Tian, W. Ratcliff, II, M. G. Kim, J.-Q. Yan, P. A. Kienzle, Q. Huang, B. Jensen, K. W. Dennis, R. W. McCallum, T. A. Lograsso, R. J. McQueeney, A. I. Goldman, J. W. Lynn and A. Kreyssig, *Phys. Rev. B*, 2010, **82**, 060514(R).
23 T. Holubar, G. Schaudy, N. Pillmayr, G. Hilscher, M. Divis and V. Nekvasil, *J. Magn. Magn. Mater*., 1992, **104–107**, 479.

Received: 23rd November 2021; Com. 21/6758