ACS
central
science

FIRST REACTIONS

Exchange Bias from Frustrated Spins

Cite This: *ACS Cent. Sci.* 2021, 7, 1295−1297

Read Online

ACCESS | Metrics & More | Article Recommendations

Elena Meirzadeh, Sae Young Han, and Xavier Roy

Geometrically frustrated lattices generate exchange bias without disorder.

The exchange bias phenomenon was first discovered in 1956 with the observation that the magnetic hysteresis loops of a sample of ferromagnetic (FM) cobalt nanoparticles were shifted along the field axis after cooling under an applied magnetic field (Figure 1).[1] It was later established that this effect occurs due to oxidation of the particle surface to form antiferromagnetic (AFM) CoO, and the resulting FM/AFM interface was identified as the source of the exchange bias effect. Since this fortuitous discovery, exchange bias in FM/AFM bilayer thin films has achieved widespread use as a key component of nonvolatile storage technologies. It is used to stabilize the magnetization of soft FM layers in readback heads and to pin the state of the spin valve at its point of maximum sensitivity.[2] Despite its importance in modern computing devices, the exact origin of exchange bias is not completely understood, though disorder-induced spin frustration is believed to play an important role.[3] The phenomenon has been thoroughly studied in magnetic bilayers, nanoparticles, and dilute magnetic alloys, but the difficulty of probing magnetic interactions at materials interfaces and in disordered systems has limited the ability to precisely control and study this property.[3] In this issue of *ACS Central Science*, Long and coauthors present the first 2D material to display intrinsic disorder-free exchange bias.[4]

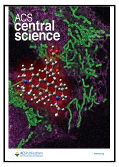
The authors propose a new strategy in which geometric frustration, rather than disorder-induced frustration, produces exchange bias in a material (Figure 2). Specifically, they designed a two-dimensional (2D) metal−organic framework material in which the metal ions are arranged in a corner-sharing triangular lattice, commonly referred to as a kagome lattice. Within each triangular unit, any two spins can align in an antiparallel configuration, but the third spin cannot align antiferromagnetically with both of its neighbors, which results in magnetic frustration. Antiferromagnetic kagome lattices generated from magnetic ions with spins of $S = 1/2$ are known to form an exotic phase of matter called a quantum spin liquid.[5] In this new study, Long and co-workers use magnetic ions with larger spins to generate a class of materials referred to as topological spin glasses, in which the freezing of disordered spins at low temperature occurs due to the geometric frustration of the lattice.

> The difficulty of probing magnetic interactions at materials interfaces and in disordered systems has limited the ability to precisely control and study this property.

The team prepared thin films of the kagome framework $Mn_3(C_6S_6)$ through an interfacial synthesis between aqueous $Mn(OAc)_2$ and benzenehexathiol dissolved in dichloromethane. The kagome lattice is enforced by the topology of the building blocks, which consists of square planar Mn^{2+} ions connected through the benzenehexathiolate ligands. The layered structure of the framework was identified using powder X-ray diffraction and scanning electron microscopy, while oxidation state assignments for the metal and ligand were confirmed using infrared and X-ray spectroscopies.

The team collected dc magnetic susceptibility measurements on a polycrystalline sample of the framework and applied a linear fit to the high temperature inverse magnetic susceptibility versus temperature data. The intersection of this line with the x-axis is referred to as the Weiss temperature (θ_W) and provides an indication of the sign (ferromagnetic

Published: July 27, 2021



ACS Publications

Published 2021 by American Chemical Society

https://doi.org/10.1021/acscentsci.1c00849

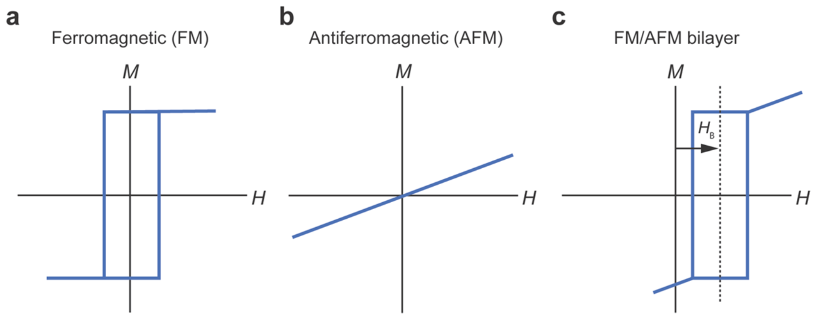


Figure 1. Magnetic moment (M) versus magnetic field (H) of (a) a ferromagnetic material and (b) an antiferromagnetic material. (c) The shifted magnetization curve generated by a FM/AFM bilayer, with the exchange bias field (H_B) indicated by the arrow.

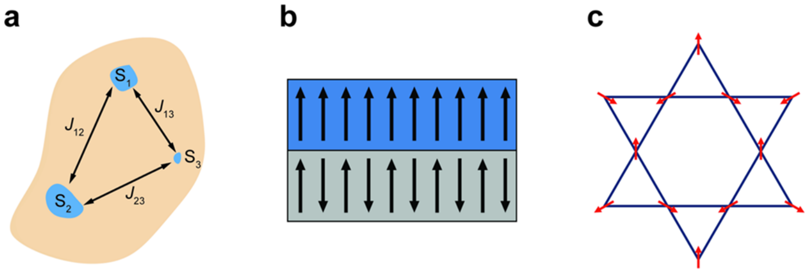


Figure 2. Illustration of (a, b) previously studied exchange bias materials versus (c) next generation. (a) Disorder-induced exchange bias in dilute magnetic alloys and (b) interfacial exchange bias from FM/AFM bilayers. (c) The design strategy developed by Long and co-workers to generate exchange bias from geometric frustration in topological spin glasses. Blue regions in (a) represent clusters of magnetic ions contained within the nonmagnetic matrix (beige).

or antiferromagnetic) and the strength of the magnetic interactions in the material. For $Mn_3(C_6S_6)$, the θ_W of −253 K revealed very strong antiferromagnetic interactions, but the susceptibility data showed no magnetic transition until a spin-freezing transition at $T_F \approx 12$ K. The large discrepancy between the Weiss temperature and spin-freezing transition can be quantified through the Ramirez[6] ratio, $f = |\theta_W|/T_F$, where the value of $f \approx 20$ for $Mn_3(C_6S_6)$ is indicative of strong magnetic frustration resulting from the kagome lattice. The team further demonstrated that the frequency dependence of the freezing transition in this material and the observation of the thermal memory effect below the freezing temperature are fully consistent with behavior expected for a spin glass.[7]

Remarkably, the team observed that upon cooling the material under a magnetic field of 1 T the subsequent magnetization curve displayed a lateral shift of −1625 Oe compared to when the material was cooled under zero field, which is characteristic of the exchange bias effect. Furthermore, a similar exchange bias could be induced by cooling the sample under a zero magnetic field and then applying a 1 T field for 1 h. This isothermal induction of exchange bias differentiates $Mn_3(C_6S_6)$ from FM/AFM bilayers, for which exchange bias can only be induced through field cooling. Importantly, the relaxation behavior of the framework is much less sensitive to time and temperature perturbations than in disordered spin glasses, indicating that the observed exchange bias originates from geometric frustration and short-range magnetic correlations, rather than from structural disorder, doping effects, or long-range magnetic interactions. The team also demonstrated that this exchange bias phenomenon is observed in another kagome topological spin glass, hydronium iron jarosite, suggesting that geometric frustration may be a general route to the design of new exchange bias materials.

> The observed exchange bias originates from geometric frustration and short-range magnetic correlations.

The observation of intrinsic exchange bias in $Mn_3(C_6S_6)$ provides new detailed insights into the general mechanisms governing the exchange bias effect and could enable the development of novel spintronic devices reliant on this phenomenon, such as energy-efficient spin valves and spin-based transistors. Moreover, the study of related kagome lattice frameworks[8] and the synthesis of new isoreticular frameworks will enrich this understanding by establishing structure−property relationships. This paves the way for the development of exchange bias materials with technologically relevant characteristics such as a larger exchange field, higher operating temperature, or electrically tunable exchange bias field. From a fundamental perspective, the ability to grow single crystals of $Mn_3(C_6S_6)$ rather than thin films would enable more direct probes of the microscopic origin of exchange bias that are not possible in interfacial or disordered materials, particularly neutron scattering measurements. The realization of intrinsic exchange bias in a 2D material is particularly significant because it opens the door to exciting new areas of investigation. For example, van der Waals spin valves may be designed by heterostructuring $Mn_3(C_6S_6)$ with a 2D magnet. The chiral magnetic structure of 2D topological spin glasses might also promote the formation of skyrmions or magnetic vortices in such heterostructures, and twisted bilayers could produce moiré lattices with exotic topological states.

Overall, this study demonstrates the ability of chemists to rationally design innovative exchange bias materials with properties that could be tailored to specific applications. We anticipate this will lead to great breakthroughs in the field.

Author Information

Corresponding Author

Xavier Roy − *Department of Chemistry, Columbia University, New York, New York 10027, United States*; orcid.org/0000-0002-8850-0725; Email: xr2114@columbia.edu

Authors

Elena Meirzadeh − *Department of Chemistry, Columbia University, New York, New York 10027, United States*

Sae Young Han − *Department of Chemistry, Columbia University, New York, New York 10027, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acscentsci.1c00849

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Meiklejohn, W. H.; Bean, C. P. New magnetic anisotropy. *Phys. Rev.* **1956**, *102*, 1413−1414.

(2) Gider, S.; Runge, B. U.; Marley, A.; Parkin, S. The magnetic stability of spin-dependent tunneling devices. *Science* **1998**, *281*, 797−799.

(3) Berkowitz, A.; Takano, K. Exchange anisotropy—a review. *J. Magn. Magn. Mater.* **1999**, *200*, 552−570.

(4) Murphy, R. A.; Darago, L. E.; Ziebel, M. E.; Peterson, E. A.; Zaia, E. W.; Mara, M. W.; Lussier, D.; Velasquez, E. O.; Shuh, D. K.; Urban, J. J.; Neaton, J. B.; Long, J. R. Exchange Bias in a Layered Metal−Organic Topological Spin Glass. *ACS Cent. Sci.* **2021**, DOI: 10.1021/acscentsci.1c00568

(5) Savary, L.; Balents, L. Quantum spin liquids: a review. *Rep. Prog. Phys.* **2017**, *80*, 016502.

(6) Ramirez, A. Strongly geometrically frustrated magnets. *Annu. Rev. Mater. Sci.* **1994**, *24*, 453−480.

(7) Mydosh, J. A. *Spin Glasses: An Experimental Introduction*; Taylor and Francis: London, 1993.

(8) Shinde, S. S.; Lee, C. H.; Jung, J. Y.; Wagh, N. K.; Kim, S. H.; Kim, D. H.; Lin, C.; Lee, S. U.; Lee, J. H. Unveiling dual-linkage 3D hexaiminobenzene metal−organic frameworks towards long-lasting advanced reversible Zn−air batteries. *Energy Environ. Sci.* **2019**, *12*, 727−738.