REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
02-12-2021	Final Report	18-Jun-2020 - 17-Jun-2021

4. TITLE AND SUBTITLE
Final Report: II.A.1.b.iii.1 Molecular Triplet Qubits

5a. CONTRACT NUMBER
W911NF-20-1-0088

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
76366-MS.2

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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RPPR Final Report
as of 27-Dec-2021

Agency Code: 21XD

Proposal Number: 76366MS **Agreement Number: W911NF-20-1-0088**
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Report Date: 17-Sep-2021 Date Received: 02-Dec-2021
Final Report for Period Beginning 18-Jun-2020 and Ending 17-Jun-2021
Title: II.A.1.b.iii.1 Molecular Triplet Qubits
Begin Performance Period: 18-Jun-2020 **End Performance Period:** 17-Jun-2021
Report Term: 0-Other

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0 **STEM Participants:**

Major Goals: 1.2. Specific Aims and Approach
Aim 1: Create modular optically addressable qubits via synthesis of discrete tunable species
- a. Synthesize rigid ligands encapsulating first-row transition metals
- b. Measure ground-state electronic structure
- c. Optically measure electronic excited-state manifold
- d. Perform optically detected EPR experiments
- e. Use DFT/ CASSCF to simulate ground state, excited state, and EPR; compare to experiment

Aim 2: Gain fundamental insight into the excited-state manifold of triplet species through hypothesis driven, rational synthetic modification.
- a. Iterate from previous results and synthesize new chemical families of synthetic targets
- b. Measure optical dynamics
- c. Parameterize and simulate finite-temperature spin dynamics
- d. Create synthetic design criteria for generating ideal excited-state manifold and dynamics

Aim 3: Embed qubits based upon design principles established in previous aims into lattices
- a. Characterize ground-state properties of lattices
- b. Characterize excited-state properties.

Accomplishments: Please see the attached pdf

Training Opportunities: Students were able to engage in collaborative discussions and participate in a large number of virtual meetings. Critically, students were able to attend "EPR school" through a virtual workshop, and attend numerous magnetism and EPR conferences virtually.

Results Dissemination: Freedman:
(123) University of North Carolina Chemistry Dept. (virtual visit) November, 2021
(122) IQUIST virtual seminar, University of Illinois October, 2021
(121) Tata Institute of Fundamental Research (TIFR), Mumbai October, 2021
(120) Center for Mechanical Control of Chemistry Seminar Series October, 2021
(119) Q-NEXT/APS workshop September, 2021
(118) CPR Horizons Conference Photonics in Chemical Physics September, 2021
(117) ACS National Meeting Atlanta (virtual) August, 2021
(116) University of Oxford's Centre for Doctoral Training in Inorganic Chemistry for Future Manufacturing June, 2021
(115) International Conference on Molecule Based Magnets Manchester, UK (virtual) June, 2021
(114) Quantum sensing workshop CQE (virtual) April, 2021
(113) University of Manchester, UK (virtual) April, 2021
(112) Naval Research Laboratory (virtual) April, 2021
(111) ACS Harry Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator (2020): Symposium Honoring Hemamala I. Karunadasa (virtual) March, 2021
(110) Uppsala University, Sweden (virtual) January, 2021
(109) AAAS Annual Meeting (virtual) January, 2021
(108) 2020 Virtual MRS Spring/Fall Meeting, live presentation December, 2020
(107) Cornell Department of Chemistry (virtual) November, 2020
(106) RSC Solid State Chemistry Group Webinars 2020 (virtual) October, 2020
(105) University of Tennessee Department of Chemistry (virtual) October, 2020
(104) 2020 CINT Annual Meeting, Los Alamos National Laboratory (virtual) September, 2020
(103) Symposium: Understanding Materials for Quantum Information Processing (virtual) August, 2020
(102) Quantum Huddle (virtual) July, 2020
Laorenza:
Quantum creators symposium

Honors and Awards: Freedman: Blavatnik Award Finalist
Laorenza: Quantum Creator award

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Danna Freedman
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Daniel Laorenza
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Michael Wojnar
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

RPPR Final Report
as of 27-Dec-2021

Partners

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I certify that the information in the report is complete and accurate:
Signature: Danna Freedman
Signature Date: 12/2/21 4:22PM

$(NR_4)_{3.5}Ga_2CA_3$

We designed and synthesized a new MOF, $(NR_4)_{3.5}Ga_2(C_6O_4Cl_2)_3$, featuring organic radical-based electronic spins on the sites of the kagomé lattice. Via post-synthetic intercalation of bulky organic cations (NR_4^+, R=Me/H, Me, Et), we are able to controllably tune the interlayer spacing between kagomé planes, allowing for deconvolution of the interlayer magnetic coupling from the stronger intralayer magnetic coupling. This magnetic characterization showed ferromagnetic coupling within the kagomé lattice and antiferromagnetic coupling between planes. This combination of exchange interactions nominates this material to host topologically interesting behavior. A manuscript reporting this study has been published in *Chemical Science* acknowledging ARO support.

Collins, K. A.; Saballos, R. J.; Fataftah, M. S.; Puggioni, D.; Rondinelli, J. M.; Freedman, D. E.Synthetic Investigation of Competing Magnetic Interactions in 2D Metal-Chloranilate Radical Frameworks *Chem. Sci.* **2020**, *11*, 5922–5928. Part of the 2020 Chemical Science HOT Article Collection

Follow up work is focused on tuning the nature of the intralayer magnetic coupling in order to switch from a ferromagnetic to antiferromagnetic kagomé lattice.

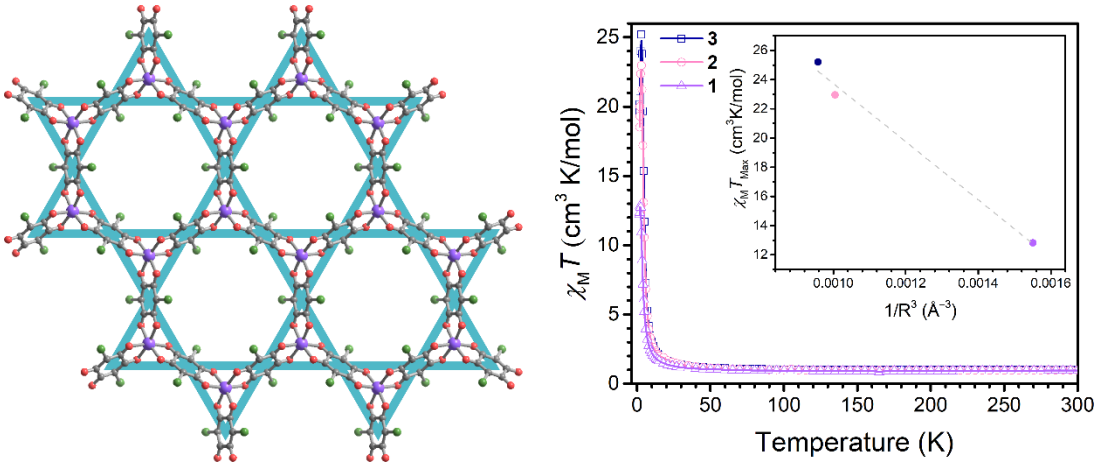

Figure 1: (Left) Crystal structure of the new kagome based material $(NMe_2H_2)_{3.5}Ga_2(C_6O_4Cl_2)_3$, with the outline of the kagome lattice formed by the radical spins on the ligand shown in blue. (Right) Magnetic susceptibility data showing the presence of ferromagnetic in these materials, as well as the dependence of the magnetic moment on the interlayer spacing.

Impact of pressure on Jarosite

Jarosite, a Cu^{2+} based mineral with a kagomé lattice, displays magnetic frustration yet orders magnetically below 65 K. We used applied pressure to smoothly vary jarosite's structure without manipulating the chemical composition, enabling a chemically invariant structure–function study. Using single-crystal and powder X-ray diffraction, we show that high applied pressures alter both the interlayer spacing and the metal–ligand bond distances. By harnessing a suite of magnetic techniques under pressure, including SQUID-based magnetometry, time-resolved synchrotron Mössbauer spectroscopy, and X-ray magnetic circular dichroism, we construct the magnetic phase diagram for jarosite up to 40 GPa. Notably, we demonstrate that the magnetic ordering temperature increases dramatically to 240 K at the highest pressures. Additionally, we conduct X-ray emission spectroscopy, Mössbauer spectroscopy, and UV–visible absorption spectroscopy experiments to comprehensively map the magnetic and electronic structures of jarosite at high pressure. We use these maps to construct chemically pure magnetostructural correlations which fully explain the nature and role of the disparate magnetic coupling interactions in jarosite. A

manuscript detailing this study was accepted in the *Journal of the American Chemical Society* acknowledging ARO support.

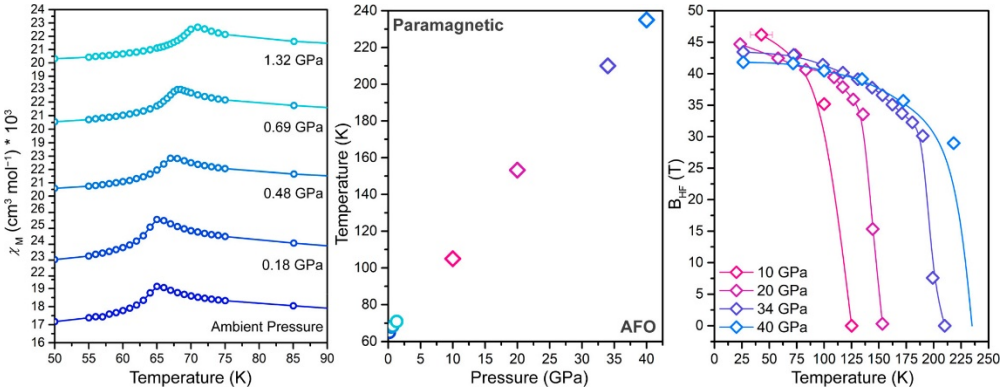

Figure 2: High pressure SQUID magnetometry (left) and synchrotron Mossbauer spectroscopy (right) show the onset of antiferromagnetic order in Jarosite with increasing pressure.

Pressure Induced Collapse of Magnetic Order in Jarosite

We observe a pressure-induced phase transition in the frustrated kagomé material jarosite at ~45 GPa, which leads to the disappearance of magnetic order. Using a suite of experimental techniques, we characterize the structural, electronic, and magnetic changes in jarosite through this phase transition. Density functional theory calculations indicate that the symmetry changes from a Rm structure transforms to the Rc space group. The resulting phase features a rare twisted kagomé lattice in which the integrity of the equilateral Fe^{3+} triangles persists. Based on symmetry arguments we hypothesize that the resulting structural changes alter the magnetic interactions to favor a possible quantum paramagnetic phase at high pressure. This work was published in *Phys. Rev. Lett.* This article will be highlighted at the Advanced Photon Source's upcoming highlight publication.

Klein, R. A.; Walsh, J. P. S.; Clarke, S. M.; Liu, Z.; Alp, E. E.; Bi, W.; Meng, Y.; Altman, A. B.; Chow, P.; Xiao, Y.; Norman, M. R.; Rondinelli, J. M.; Jacobsen, S. D.; Puggioni, D.; Freedman, D. E. Pressure Induced Collapse of Magnetic Order in Jarosite *Phys. Rev. Lett.* **2020**, *125*, 077202.

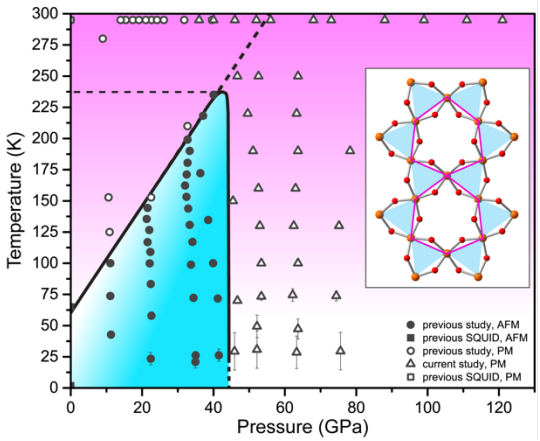

Figure 3: Magnetic phase diagram developed for jarosite, illustrating the collapse of magnetic order.

$BiVO_3$

We discovered $BiVO_3$, one of the missing bismuth–TM perovskites (Figure 2). DFT calculations predict that this phase is a rare example of a metallic antiferromagnet. Excitingly, this phase can be completely recovered to ambient pressure. A manuscript reporting these results was published *Physical Review Materials*, acknowledging ARO support.[2] We are currently pursuing bulk characterization methods on samples of $BiVO_3$ isolated from large volume hydraulic press syntheses.

Klein, R. A.; Altman, A. B.; Saballos, R. J.; Walsh, J. P. S.; Tamerius, A. D.; Meng, Y.; Puggioni, D.; Jacobsen, S. D.; Rondinelli, J. M.; Freedman, D. E. High-Pressure Synthesis of the BiVO3 Perovskite *Phys. Rev. Mater.* **2019**, *3*, 64411.

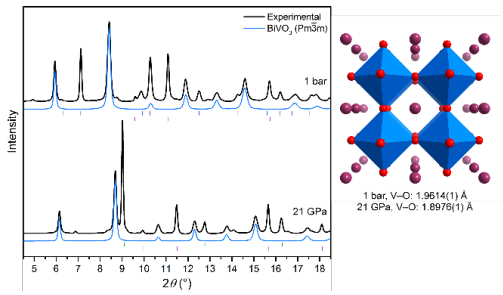

Figure 4: Crystal structure of $BiVO_3$, a previously missing perovskite in the $BiMO_3$ family.

Ongoing projects

The Cu^{2+} hydroxychloride family of minerals, the atacamites, is a class of materials with nontrivial magnetic ground-states. Characterization of the magnetic ground states of each member of the family requires the isolation of pure samples. Towards this end, we utilized the tunability afforded by hydrothermal chemistry for the controlled synthesis of different phases in the atacamite family. We are currently working on a manuscript detailing our synthetic findings.

Ongoing Projects

One-Dimensional Spin Chains

One-dimensional spin chains host quasiparticles known as spinons which are the fractionalized particle of an electron that has spin but not charge. Spin chains of antiferromagnetically coupled $S = ½$ spins are known as quantum spin chains and are capable of generating a spin current due to these spinons. We synthesized and characterized a new family of one-dimensional spin chains, M(en)(DPhA), where en is ethylenediamine and $DPhAH_2$ is the ligand 2,5-bis(diphenylmethyl)-3,6-dihydroxy-*p*-benzoquinone. In this system the metal can be either diamagnetic (In (III)) or paramagnetic (Mn (II), high spin Fe (III), Co (II), or Ni (II)). For the iron and indium congeners, the ligand hosts a stable organic radical. The indium chain is a purely $S = ½$ chain with ferromagnetic coupling between the ligand radicals. In order to determine whether metal and ligand spins are antiferromagnetically coupled, we investigated the magnetic coupling present in the iron chain as a model system. We measured strong antiferromagnetic coupling between the $S = 5/2$ Fe(III) and $S = ½$ ligand spins (-75 cm^{-1}), and we are currently working on synthesizing a congener of the chain with an $S = ½$ metal such as low spin Fe (III) or Cu (II).

Organic Radical Based Sawtooth Lattices

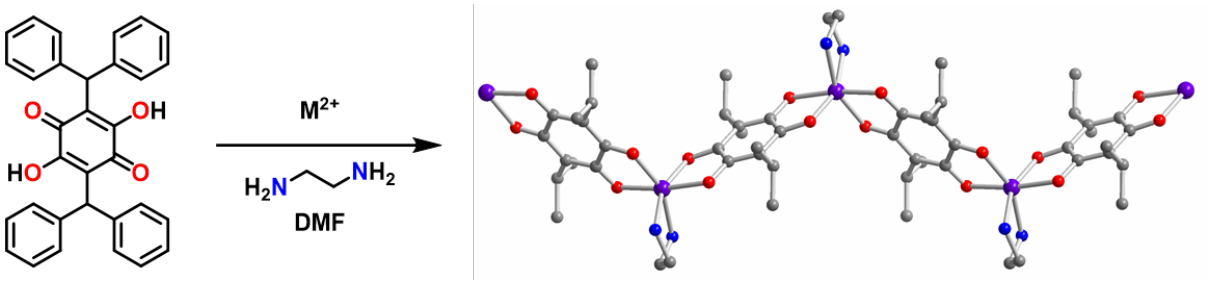

Figure 5: (Left) Chemical structure of the ligand 2,5-bis(diphenylmethyl)-3,6-dihydroxy-*p*-benzoquinone and the synthetic scheme that results in the formation of M(en)(DPhA) **(Right)** Crystal structure of M(en)(DPhA). Phenyl groups of DPhA have been omitted for clarity. Dark gray, red, and purple spheres are carbon, oxygen, and the metal ion, respectively.

In the M(en)(DPhA) family of materials, the terminal non-bridging ligand is tunable beyond ethylenediamine, and we have synthesized chains capped instead with 2,2'-bipyridine and 1,10-phenanthroline. We are now pursuing the incorporation of terminal bidentate ligands that host stable organic radicals, such as semiquinones and 1,10-phenanthroline-5,6-dione, with chains of diamagnetic metals. If both the bridging ligand and the capping ligand host an organic radical, this creates an electronic sawtooth lattice, a 1D system theorized to give rise to magnetic frustration.

Dimensionality in the Nickel Oxalate System

We synthesized and structurally characterized two new nickel oxalate-based materials, a 1D chain material, $(H_2NMe_2)_2Ni(C_2O_4)_2$, and a 3D hyper-honeycomb framework, $(HNEt_3)_2Ni_2(C_2O_4)_3$. Preliminary magnetic

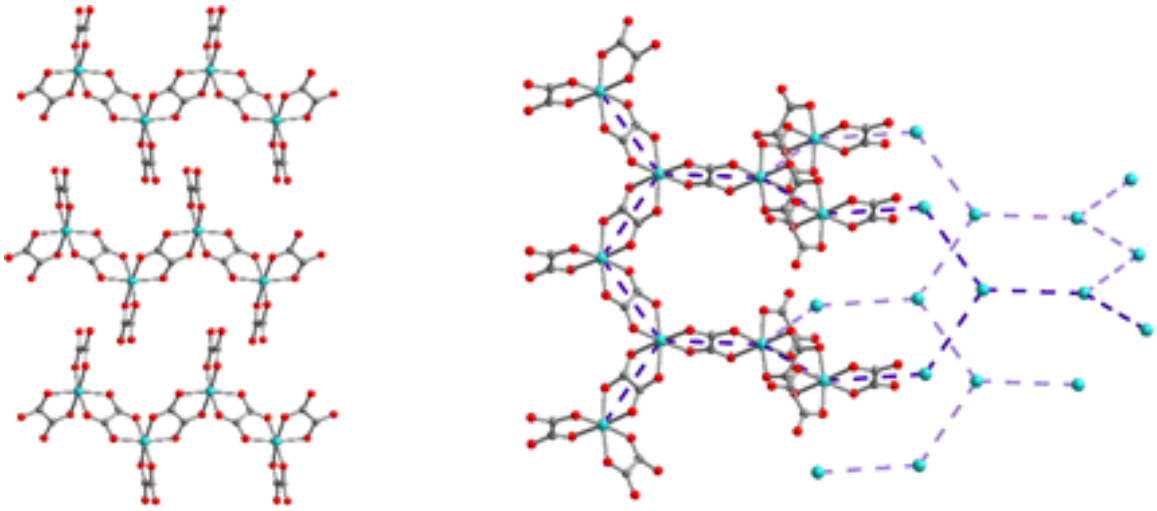

Figure 6: (Left) Crystal structure of the new 1D nickel oxalate chain, $(H_2NMe_2)_2Ni(C_2O_4)_2$. The dimethylammonium counter-cations have been omitted for clarity. **(Right)** Crystal structure of the new 3D nickel oxalate hyper-honeycomb material, $(HNEt_3)_2Ni_2(C_2O_4)_3$. The purple dashed lines are guides for the eye and highlight the extended 3D network. Triethylammonium counter-cations have been omitted for clarity. Dark gray, red, and light teal spheres are carbon, oxygen, and nickel, respectively.

characterization of the 1D chain shows unusual low-temperature behavior while the 3D species has potential metamagnetic behavior.

Future work consists of follow-up experiments to further probe the abnormal low-temperature behavior of the 1D system and the metamagnetism in the 3D material. We are also working towards synthesizing the analogous 2D honeycomb framework of the series.

Towards a Magnetic Stuffed Honeycomb Lattice

We are synthetically targeting the magnetic lattice-type known as the stuffed honeycomb lattice, where competing coupling interactions ($\boldsymbol{J}_1$ and $\boldsymbol{J}_2$) lead to an emergent lattice. This lattice topology has been implicated in the spin liquidity of $LiZn_2Mo_3O_8$. Towards this end, we propose synthesizing a metal-organic-based system wherein paramagnetic complexes are incorporated within the hexagonal pores of a 2D honeycomb lattice. We synthesized the $S = ½$ $Cu_2(pymca)_3ClO_4$ and $S = 1$ $Ni_2(pymca)_3OH \cdot H_2O$ (pymca = 2-carboxy-pyrimidine) honeycomb frameworks, following literature syntheses. For our paramagnetic complexes, we synthesized tetrachlorometallates(II) of the series $(NEt_4)_2MCl_4$ (M = Cu^{2+}, Ni^{2+}). It is proposed that the electrostatic attraction between the anionic complexes and the cationic framework will provide a favorable driving force for complex incorporation.

Future work is focused on incorporation of the paramagnetic complexes within the frameworks' pores to access a stuffed honeycomb lattice.

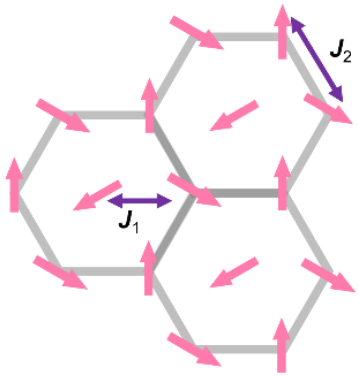

Figure 7: Schematic of the stuffed honeycomb lattice where $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$ denote coupling between incorporated spins and lattice spins and coupling between lattice spins, respectively. The relationship $\boldsymbol{J}_1/\boldsymbol{J}_2$ in this lattice-type leads to emergent behavior. Spins denoted by pink arrows.

References

1) Collins, K. A.; Saballos, R. J.; Fataftah, M. S.; Puggioni, D.; Rondinelli, J. M.; Freedman, D. E.Synthetic Investigation of Competing Magnetic Interactions in 2D Metal-Chloranilate Radical Frameworks *Chem. Sci.* **2020**, *11*, 5922–5928.
2) Klein, R. A.; Altman, A. B.; Saballos, R. J.; Walsh, J. P. S.; Tamerius, A. D.; Meng, Y.; Puggioni, D.; Jacobsen, S. D.; Rondinelli, J. M.; Freedman, D. E. *Phys. Rev. Mater.* **2019**, *3*, 64411.
3) Klein, R. A.; Walsh, J. P. S; Clarke, S. M.; Guo, Y.; Bi, W.; Fabbris, G.; Meng, Y.; Haskel, D.; Alp, E. E.; Van Duyne, R. P.; Jacobsen, S. D.; Freedman, D. E. *J. Am. Chem. Soc.* **2018**, *140*, 12001–12009.
4) Klein, R. A.; Walsh, J. P. S.; Clarke, S. M.; Liu, Z.; Alp, E. E.; Bi, W.; Meng, Y.; Altman, A. B.; Chow, P.; Xiao, Y.; Norman, M. R.; Rondinelli, J. M.; Jacobsen, S. D.; Puggioni, D.; Freedman, D. E. Pressure Induced Collapse of Magnetic Order in Jarosite *Phys. Rev. Lett.* **2020**, *125*, 077202.