



HAL
open science

Introduction to order, disorder and ultrafast phenomena in functional solids

H. Tokoro, Eric Collet, Ernest Pastor

► To cite this version:

H. Tokoro, Eric Collet, Ernest Pastor. Introduction to order, disorder and ultrafast phenomena in functional solids. *Materials Advances*, 2024, 5 (17), pp.6686-6689. 10.1039/d4ma90097a . hal-04688944

HAL Id: hal-04688944

<https://hal.science/hal-04688944v1>

Submitted on 5 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



Cite this: *Mater. Adv.*, 2024,
5, 6686

DOI: 10.1039/d4ma90097a

rsc.li/materials-advances

Introduction to order, disorder and ultrafast phenomena in functional solids

Hiroko Tokoro,^a Eric Collet^{b,c} and Ernest Pastor^{b,c}

Disorder in solids manifests in the variable extended loss of the translational symmetry.^{1,2} This change in the crystallographic properties can dramatically impact the solid's functionality by

altering its electric conduction, magnetic response or optical properties.^{3–7} Consequently, manipulating disorder *via* the targeted control of defect populations is central to developing new functional materials, such as those used for catalysis and magnetic memories,^{8–13} or in energy and thermal storage, as discussed in this collection by Kubota *et al.* (<https://doi.org/10.1039/D3MA01162C>).

Disorder is particularly important for materials that undergo photo-induced phase transformations as, often, light excitation triggers a change in the way the system is ordered.¹⁴ For example, photoexcitation of $\text{Sr}_3\text{Ir}_2\text{O}_7$ or

$\text{RbMnFe}(\text{CN})_6$ can change magnetic spin order and induce a transition from antiferromagnetic to paramagnetic, or ferromagnetic to antiferromagnetic.^{15–18} Similarly, in the ferroelectric solid TTF-CA, thermal or photoexcitation can induce a change in polar order and affect the ferroelectric properties.^{19–23}

These light-active phase-change materials hold incredible technological potential as they offer the possibility to achieve transformation speeds not attainable using thermodynamical tools (*i.e.*, heating or increasing pressure) thus opening the door to ultra-fast switches or memories. Currently, great research

^a Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8577, Japan.

^b Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) – UMR 6251, 35000 Rennes, France.

^c CNRS, Univ Rennes, DYNACOM (Dynamical Control of Materials Laboratory) – IRL2015, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan

^c CNRS, Univ Rennes, DYNACOM (Dynamical Control of Materials Laboratory) – IRL2015, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan



Hiroko Tokoro

Hiroko Tokoro is a Professor of Materials Science at the University of Tsukuba. She received BS from Keio University, ME from Kyoto University, and PhD from the University of Tokyo. Her career includes working as a JSPS fellowship (2004–2007) and JST researcher (2007–2010), serving as an Assistant Professor at the University of Tokyo (2011–2013), and holding the position of Associate Professor at University of Tsukuba (2013–2018). She has received awards, including the German Innovation Award (2016) and the Yonezawa Memorial Prize of JPS (2020). Her research mainly focuses on bistability and phase transition in solid-state materials.



Eric Collet

Eric Collet is Professor of Physics at the University of Rennes, elected at the Academy of Europe. He has a chair at the Institut Universitaire de France for fundamental research. He is co-directing the International Research Laboratory “Dynamical Control of Materials”, funded by CNRS, the University of Rennes and the University of Tokyo. His research topics are about functional materials, phase transitions and out-of-equilibrium dynamics. He received the 2022 Alajos Kálmán Prize of the European Crystallographic Association, the 2020 Silver Medal of CNRS and the 2017 Louis Ancel prize, condensed matter prize of the French Physical Society.



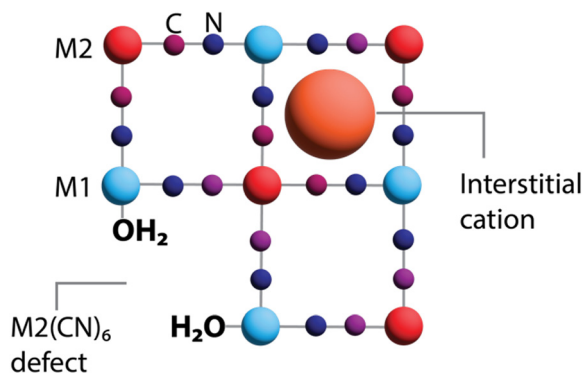


Fig. 1 Two type of defects that can emerge in Prussian blue analogues (PBA) of formula $A_xM_1y[M_2(CN)_6]_n \cdot xH_2O$ (A = alkaline), and which affect the function of the material.

efforts are devoted to understanding photo-induced transformations with growing evidence highlighting the critical role that disorder plays in enabling control of the phase change.^{24–28} The development of tools capable of elucidating the impact of defects in the ground state and upon excitation, from microscopic to macroscopic scales, is crucial to enable further technological developments.

Defects can take many different shapes and forms. For example, in Prussian blue analogues (PBA), with structure $A_xM_1y[M_2(CN)_6]_n \cdot xH_2O$ (A = alkaline), disorder might be chemically controlled through $M_2(CN)_6$ vacancies and variable quantities of water molecules, as well as due to the presence of different interstitial cations, amongst other sources (Fig. 1).^{29,30} These defects can partake in the collective intermetallic charge transfer, which can be driven by external stimuli such as temperature or pressure.^{6,31–34}

Defects can also be generated upon illumination.^{35–38} As shown by Hervé *et al.*

(<https://doi.org/10.1039/D3MA01072D>), in the case of PBA, the excitation of the solid can induce a charge transfer at the microscopic scale, causing a local structural distortion around the metal ion known as a polaron (Fig. 2).^{37,39–42} These photoinduced polarons are important because they are the heart of cooperative photo-active phenomena that might enable the magnification of external stimuli towards a macroscopic charge-transfer phase transition.^{28,43–45}

Similarly, in bistable molecular solids, such as spin crossover materials, the constituting molecules may be thermally or optically converted from one electronic state to another in a collective way. However, fluctuations in the balance between elastic interactions and entropy can lead to the long-range ordering or disordering of molecules in different spin states, causing stepwise thermal conversion to emerge, and therefore multi-stable phases.^{46–49} For many spin-transition materials, stepwise transitions

are associated with long-range ordering of molecules in different spin states and are therefore symmetry-breaking, which also allows for a magneto-electric effect.⁵⁰ The case of order-disorder of molecules in different spin states, without symmetry-breaking, is discussed in this collection by Ruzzi *et al.* (<https://doi.org/10.1039/D3MA01057K>).

Optical methods, relying on recent advances in laser and detection tools, offer a great platform to characterise the role of disorder and expose the complex interplay of phenomena that leads to phase metastability. The probes can provide information on changes in local and/or long-range order. For example, spectroscopic methods can be used to track the fingerprints of ground-state defects and impulsive spectroscopy can resolve, with unprecedented time resolution, how the electronic and structural systems of the solid couple and become disordered upon excitation.^{26,51–53} As shown by Sugisawa *et al.* (<https://doi.org/10.1039/D3MA00317E>), methods like time-resolved reflectance and second-harmonic generation can be used to reveal how photo-excitation modulates the polarisation structure of hydrogen-bonded ferroelectric materials relevant for technological applications.

Importantly, it is now possible to perform such optical experiments under in-situ-like conditions thus characterising the response of the solid under technologically relevant temperature, pressure and excitation regimes.⁵⁴ For example, in this collection, Dronova *et al.* use variable-temperature infrared spectroscopy to learn about the interactions between cations and the cyanide-bridge networks in PBA (<https://doi.org/10.1039/D4MA00064A>).

Similarly, structural and coherent imaging methods, powered by unprecedented developments in large-scale facilities, offer the possibility to visualise the formation of defects in real time.^{55,56} In this regard, the measurement of weak diffuse signals that track random displacements in the solid's structure is exposing, not only that defects are important, but that time-dependent, spatial interaction between defects can dictate the phase of the system upon



Ernest Pastor

Dr Ernest Pastor is a CNRS Junior Professor at The Institute of Physics of Rennes (IPR). His research focuses on characterising solids for solar-energy conversion using optical, electrochemical and time-resolved X-ray methods. He is particularly interested in understanding and controlling the role of disorder in catalytic solids. Photo by Frédéric Obé.



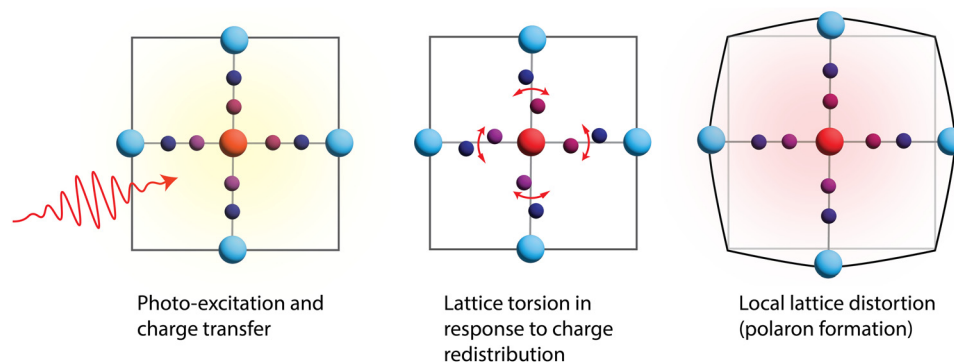


Fig. 2 Formation of a photo-induced polaron in a PBA. The local structural distortion can be the precursor of cooperative phenomena in the solid that magnifies the effect of the external perturbation.

irradiation.⁵⁷ The use of coherent imaging to capture polaronic states is discussed in this collection by Sarkar *et al.* (<https://doi.org/10.1039/D4MA00154K>). Further development of experimental and theoretical methods to understand and analyse such signals promises to reveal unexpected physicochemical phenomena that could be useful to manipulate solids on demand. However, due to the multiscale nature of photoinduced processes, theoretical developments are very challenging.

In this themed collection we highlight works focusing on the implementation of advanced experimental tools to characterize defects and the development of robust theoretical frameworks to understand the role of disorder. Further advances in these areas are needed to push the boundaries of optical control of materials. However, the recent developments in laser techniques, large-scale facilities and computational capabilities offer an exciting outlook for the characterisation and control of disorder in functional solids.

As guest editors, we would like to thank all the authors that have contributed as well as the RSC editorial team for their help in coordinating the effort. We hope the research highlighted in this collection will be useful for the multiple communities seeking to understand and control disorder in solids in order to instil new functionality that powers the technologies of the future.

References

- 1 A. M. S. W. Hayes, *Defects and Defect Processes in Nonmetallic Solids*, Dover Publications, 2004.
- 2 C. R. A. Catlow, in *Defects and Disorder in Crystalline and Amorphous Solids*, ed. C. R. A. Catlow, Springer Netherlands, Dordrecht, 1994, pp. 1–23.
- 3 E. Pastor, M. Sachs, S. Selim, J. R. Durrant, A. A. Bakulin and A. Walsh, *Nat. Rev. Mater.*, 2022, 7, 503–521.
- 4 E. Pastor, L. Montañés, A. Gutiérrez-Blanco, F. S. Hegner, C. A. Mesa, N. López and S. Giménez, *Nanoscale*, 2022, 14, 15596–15606.
- 5 A. K. Cheetham, T. D. Bennett, F.-X. Coudert and A. L. Goodwin, *Dalton Trans.*, 2016, 45, 4113–4126.
- 6 H. Tokoro and S. Ohkoshi, *Bull. Chem. Soc. Jpn.*, 2015, 88, 227–239.
- 7 E. Janod, J. Tranchant, B. Corraze, M. Querré, P. Stoliar, M. Rozenberg, T. Cren, D. Roditchev, V. T. Phuoc, M.-P. Besland and L. Cario, *Adv. Funct. Mater.*, 2015, 25, 6287–6305.
- 8 S. Kim, J. S. Park and A. Walsh, *ACS Energy Lett.*, 2018, 3, 496–500.
- 9 S. Selim, E. Pastor, M. García-Tecedor, M. R. Morris, L. Francàs, M. Sachs, B. Moss, S. Corby, C. A. Mesa, S. Gimenez, A. Kafizas, A. A. Bakulin and J. R. Durrant, *J. Am. Chem. Soc.*, 2019, 141, 18791–18798.
- 10 Z. Meng, E. Pastor, S. Selim, H. Ning, M. Maimaris, A. Kafizas, J. R. Durrant and A. A. Bakulin, *J. Am. Chem. Soc.*, 2023, 145, 17700–17709.
- 11 S. Bai, N. Zhang, C. Gao and Y. Xiong, *Nano Energy*, 2018, 53, 296–336.
- 12 H. Tokoro, M. Yoshikiyo, K. Imoto, A. Namai, T. Nasu, K. Nakagawa, N. Ozaki, F. Hakoe, K. Tanaka, K. Chiba, R. Makiura, K. Prassides and S. Ohkoshi, *Nat. Commun.*, 2015, 6, 7037.
- 13 S. Ohkoshi, K. Nakagawa, M. Yoshikiyo, A. Namai, K. Imoto, Y. Nagane, F. Jia, O. Stefanczyk, H. Tokoro, J. Wang, T. Sugahara, K. Chiba, K. Motodohi, K. Isogai, K. Nishioka, T. Momiki and R. Hatano, *Nat. Commun.*, 2023, 14, 8466.
- 14 S. Wall, S. Yang, L. Vidas, M. Chollet, J. M. Glowia, M. Kozina, T. Katayama, T. Henighan, M. Jiang, T. A. Miller, D. A. Reis, L. A. Boatner, O. Delaire and M. Trigo, *Science*, 2018, 362, 572–576.
- 15 E. Pastor, D. Moreno-Mencia, M. Monti, A. S. Johnson, N. Fleischmann, C. Wang, Y. Shi, X. Liu, D. G. Mazzone, M. P. M. Dean and S. Wall, *Phys. Rev. B*, 2022, 105, 064409.
- 16 G. Azzolina, H. Tokoro, K. Imoto, M. Yoshikiyo, S. Ohkoshi and E. Collet, *Angew. Chem., Int. Ed.*, 2021, 60, 23267–23273.
- 17 D. G. Mazzone, D. Meyers, Y. Cao, J. G. Vale, C. D. Dashwood, Y. Shi, A. J. A. James, N. J. Robinson, J. Lin, V. Thampany, Y. Tanaka, A. S. Johnson, H. Miao, R. Wang, T. A. Assefa, J. Kim, D. Casa, R. Mankowsky, D. Zhu, R. Alonso-Mori, S. Song, H. Yavas, T. Katayama, M. Yabashi, Y. Kubota, S. Owada, J. Liu, J. Yang, R. M. Konik, I. K. Robinson, J. P. Hill, D. F. McMorrow, M. Först, S. Wall, X. Liu and M. P. M. Dean, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, 118, e2103696118.
- 18 H. Tokoro, T. Matsuda, T. Nuida, Y. Moritomo, K. Ohoyama, E. D. L. Dangui, K. Boukheddaden and



- S. Ohkoshi, *Chem. Mater.*, 2008, **20**, 423–428.
- 19 E. Collet, *Science*, 2003, **300**, 612–615.
- 20 M. H. Lemée-Cailleau, M. Le Cointe, H. Cailleau, T. Luty, F. Moussa, J. Roos, D. Brinkmann, B. Toudic, C. Ayache and N. Karl, *Phys. Rev. Lett.*, 1997, **79**, 1690–1693.
- 21 S. Koshihara, Y. Tokura, T. Mitani, G. Saito and T. Koda, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1990, **42**, 6853–6856.
- 22 S. Koshihara, Y. Takahashi, H. Sakai, Y. Tokura and T. Luty, *J. Phys. Chem. B*, 1999, **103**, 2592–2600.
- 23 S.-Q. Su, S.-Q. Wu, S. Kanegawa, K. Yamamoto and O. Sato, *Chem. Sci.*, 2023, **14**, 10631–10643.
- 24 A. Zong, A. Kogar, Y.-Q. Bie, T. Rohwer, C. Lee, E. Baldini, E. Ergeçen, M. B. Yilmaz, B. Freelon, E. J. Sie, H. Zhou, J. Straquadine, P. Walmsley, P. E. Dolgirev, A. V. Rozhkov, I. R. Fisher, P. Jarillo-Herrero, B. V. Fine and N. Gedik, *Nat. Phys.*, 2019, **15**, 27–31.
- 25 G. A. de la Peña Muñoz, A. A. Correa, S. Yang, O. Delaire, Y. Huang, A. S. Johnson, T. Katayama, V. Krapivin, E. Pastor, D. A. Reis, S. Teitelbaum, L. Vidas, S. Wall and M. Trigo, *Nat. Phys.*, 2023, **19**, 1489–1494.
- 26 A. S. Johnson, D. Moreno-Mencía, E. B. Amuah, M. Menghini, J.-P. Locquet, C. Giannetti, E. Pastor and S. E. Wall, *Phys. Rev. Lett.*, 2022, **129**, 255701.
- 27 M. Fechner, M. Först, G. Orenstein, V. Krapivin, A. S. Disa, M. Buzzi, A. von Hoegen, G. de la Pena, Q. L. Nguyen, R. Mankowsky, M. Sander, H. Lemke, Y. Deng, M. Trigo and A. Cavalleri, *Nat. Mater.*, 2024, **23**, 363–368.
- 28 M. Hervé, G. Privault, E. Trzop, S. Akagi, Y. Watier, S. Zerdane, I. Chaban, R. G. Torres Ramirez, C. Mariette, A. Volte, M. Cammarata, M. Levantino, H. Tokoro, S. Ohkoshi and E. Collet, *Nat. Commun.*, 2024, **15**, 267.
- 29 H. Tokoro and S. Ohkoshi, *Dalton Trans.*, 2011, **40**, 6825–6833.
- 30 H. L. B. Boström and W. R. Brant, *J. Mater. Chem. C*, 2022, **10**, 13690–13699.
- 31 S. Ohkoshi and H. Tokoro, *Acc. Chem. Res.*, 2012, **45**, 1749–1758.
- 32 J. Zimara, H. Stevens, R. Oswald, S. Demeshko, S. Dechert, R. A. Mata, F. Meyer and D. Schwarzer, *Inorg. Chem.*, 2021, **60**, 449–459.
- 33 L. Trinh, S. Zerdane, S. Mazérat, N. Dia, D. Dragoe, C. Herrero, E. Rivière, L. Catala, M. Cammarata, E. Collet and T. Mallah, *Inorg. Chem.*, 2020, **59**, 13153–13161.
- 34 C. R. Gros, M. K. Peprah, B. D. Hosterman, T. V. Brinzari, P. A. Quintero, M. Sendova, M. W. Meisel and D. R. Talham, *J. Am. Chem. Soc.*, 2014, **136**, 9846–9849.
- 35 L. M. Carneiro, S. K. Cushing, C. Liu, Y. Su, P. Yang, A. P. Alivisatos and S. R. Leone, *Nat. Mater.*, 2017, **16**, 819–825.
- 36 E. Pastor, J.-S. Park, L. Steier, S. Kim, M. Grätzel, J. R. Durrant, A. Walsh and A. A. Bakulin, *Nat. Commun.*, 2019, **10**, 3962.
- 37 S. Biswas, S. Wallentine, S. Bandaranayake and L. R. Baker, *J. Chem. Phys.*, 2019, **151**, 104701.
- 38 I. J. Porter, S. K. Cushing, L. M. Carneiro, A. Lee, J. C. Ondry, J. C. Dahl, H.-T. Chang, A. P. Alivisatos and S. R. Leone, *J. Phys. Chem. Lett.*, 2018, **9**, 4120–4124.
- 39 J. S. P. Cresi, L. D. Mario, D. Catone, F. Martelli, A. Paladini, S. Turchini, S. D'Addato, P. Luches and P. O'Keeffe, *J. Phys. Chem. Lett.*, 2020, **11**, 5686–5691.
- 40 C. Franchini, M. Reticioli, M. Setvin and U. Diebold, *Nat. Rev. Mater.*, 2021, **6**, 560–586.
- 41 J. Wiktor and A. Pasquarello, *ACS Appl. Mater. Interfaces*, 2019, **11**, 18423–18426.
- 42 Y.-J. Kim, J. L. Mendes, J. M. Michelsen, H. J. Shin, N. Lee, Y. J. Choi and S. K. Cushing, *Sci. Adv.*, 2024, **10**, eadk4282.
- 43 G. Azzolina, R. Bertoni, C. Ecolivet, H. Tokoro, S. Ohkoshi and E. Collet, *Phys. Rev. B*, 2020, **102**, 134104.
- 44 R. Bertoni, M. Lorenc, H. Cailleau, A. Tissot, J. Laisney, M.-L. Boillot, L. Stoleriu, A. Stancu, C. Enachescu and E. Collet, *Nat. Mater.*, 2016, **15**, 606–610.
- 45 S. Zerdane, M. Hervé, S. Mazerat, L. Catala, R. Alonso-Mori, J. M. Glowina, S. Song, M. Levantino, T. Mallah, M. Cammarata and E. Collet, *Faraday Discuss.*, 2022, **237**, 224–236.
- 46 G. Molnár, S. Rat, L. Salmon, W. Nicolazzi and A. Bousseksou, *Adv. Mater.*, 2018, **30**, 1703862.
- 47 A. Volte, C. Mariette, R. Bertoni, M. Cammarata, X. Dong, E. Trzop, H. Cailleau, E. Collet, M. Levantino, M. Wulff, J. Kubicki, F.-L. Yang, M.-L. Boillot, B. Corraze, L. Stoleriu, C. Enachescu and M. Lorenc, *Commun. Phys.*, 2022, **5**, 168.
- 48 D. Chernyshov, H.-B. Bürgi, M. Hostettler and K. W. Törnroos, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 094116.
- 49 G. Azzolina, R. Bertoni and E. Collet, *J. Appl. Phys.*, 2021, **129**, 085106.
- 50 V. B. Jakobsen, E. Trzop, E. Dobbelaar, L. C. Gavin, S. Chikara, X. Ding, M. Lee, K. Esien, H. Müller-Bunz, S. Felton, E. Collet, M. A. Carpenter, V. S. Zapf and G. G. Morgan, *J. Am. Chem. Soc.*, 2022, **144**, 195–211.
- 51 E. Pastor, Z. Lian, L. Xia, D. Ecija, J. R. Galán-Mascarós, S. Barja, S. Giménez, J. Arbiol, N. López and F. P. García de Arquer, *Nat. Rev. Chem.*, 2024, **8**, 159–178.
- 52 S. Wall, D. Wegkamp, L. Foglia, K. Appavoo, J. Nag, R. F. Haglund, J. Stähler and M. Wolf, *Nat. Commun.*, 2012, **3**, 721.
- 53 K. Barlow and J. O. Johansson, *Phys. Chem. Chem. Phys.*, 2021, **23**, 8118–8131.
- 54 G. Privault, G. Huitric, M. Hervé, E. Trzop, J. Tranchant, B. Corraze, Z. Khaldi, L. Cario, E. Janod, J.-C. Ameline, N. Godin and R. Bertoni, *Eur. Phys. J.: Spec. Top.*, 2023, **232**, 2195–2203.
- 55 A. S. Johnson, D. Perez-Salinas, K. M. Siddiqui, S. Kim, S. Choi, K. Volckaert, P. E. Majchrzak, S. Ulstrup, N. Agarwal, K. Hallman, R. F. Haglund, C. M. Günther, B. Pfau, S. Eisebitt, D. Backes, F. Maccherozzi, A. Fitzpatrick, S. S. Dhesi, P. Gargiani, M. Valvidares, N. Artrith, F. de Groot, H. Choi, D. Jang, A. Katoch, S. Kwon, S. H. Park, H. Kim and S. E. Wall, *Nat. Phys.*, 2023, **19**, 215–220.
- 56 D. A. Keen and A. L. Goodwin, *Nature*, 2015, **521**, 303–309.
- 57 A. S. Johnson, E. Pastor, S. Batlle-Porro, H. Benzidi, T. Katayama, G. A. de la Peña Muñoz, V. Krapivin, S. Kim, N. López, M. Trigo and S. E. Wall, *Nat. Phys.*, 2024, **20**, 970–975.

