

Foreword: Ultrafast Phenomena in condensed matter physics

Eric Collet, S. Ravy

▶ **To cite this version:**

Eric Collet, S. Ravy. Foreword: Ultrafast Phenomena in condensed matter physics. Comptes Rendus. Physique, 2021, 22 (S2), pp.3-14. 10.5802/crphys.88 . hal-03556788

HAL Id: hal-03556788
https://hal.science/hal-03556788

Submitted on 4 Feb 2022

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

INSTITUT DE FRANCE
Académie des sciences

Comptes Rendus

Physique

Eric Collet and Sylvain Ravy

Foreword: Ultrafast Phenomena in condensed matter physics

Volume 22, issue S2 (2021), p. 3-14

<https://doi.org/10.5802/crphys.88>

Part of the Special Issue: Physics of ultra-fast phenomena

Guest editors: Éric Collet (Université Rennes 1, CNRS, France) and Sylvain Ravy (Université Paris-Saclay, CNRS, France)

© Académie des sciences, Paris and the authors, 2021.
Some rights reserved.

This article is licensed under the
Creative Commons Attribution 4.0 International License.
http://creativecommons.org/licenses/by/4.0/

Les Comptes Rendus. Physique *sont membres du*
Centre Mersenne pour l'édition scientifique ouverte
www.centre-mersenne.org

Comptes Rendus
Physique
2021, 22, nº S2, p. 3-14
https://doi.org/10.5802/crphys.88

Foreword / *Avant-propos*

Foreword: Ultrafast Phenomena in condensed matter physics

Avant-propos : Phénomènes ultra-rapides en physique de la matière condensée

Eric Collet *, *a* **and Sylvain Ravy** *, *b*

a Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France
URL: https://ipr.univ-rennes1.fr/interlocuteurs/eric-collet

b Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France
URL: https://www.lps.u-psud.fr/spip.php?article531

E-mails: eric.collet@univ-rennes1.fr (E. Collet), sylvain.ravy@universite-paris-saclay.fr (S. Ravy)

Abstract. Matter is dynamic and changes under the effect of various external constraints, in particular light. The development of ultra-fast techniques now makes it possible to study the elementary mechanisms of ultrafast photoinduced phenomena, in particular by following the dynamics of electronic and structural degrees of freedom of matter. These studies provide a better understanding of these non-equilibrium processes in order to control the physical properties of molecules and materials by light. In this introductory article we discuss different aspects of studying ultra-fast condensed matter phenomena.

Résumé. La matière est dynamique et se transforme sous l'effet de différentes contraintes extérieures, en particulier la lumière. Le développement de techniques ultra-rapides permet à présent d'étudier les mécanismes élémentaires de phénomènes photoinduits ultra-rapides, en particulier en suivant les dynamiques des degrés de libertés électroniques et structuraux de la matière. Ces études permettent de mieux comprendre ces processus hors équilibre pour envisager un contrôle des propriétés physiques de molécules et matériaux par la lumière. Dans cet article d'introduction nous abordons différents aspects de l'étude de phénomènes ultra-rapide en matière condensée.

Keywords. Condensed matter, Molecules, Materials, Ultra-fast phenomena, Out-of-equilibrium, Spectroscopies, Diffraction.

Mots-clés. Matière Condensée, Molécules, Matériaux, Phénomènes ultra-rapides, Hors équilibre, Spectroscopies, Diffraction.

* Corresponding authors.

For understanding the physical properties of molecules or materials, it is necessary to investigate how the constituting degrees of freedom (spin, charge, orbital, molecular structure or crystalline packing, Figure 1) equilibrate and get ordered at microscopic scales. At thermal equilibrium, these orders may change under the effect of external parameters such as pressure and temperature, which may transform molecules or drive phase transitions. More recently, new challenges have emerged to direct the functionality of condensed matter, as excitation with an ultrashort laser pulse allows for driving ultrafast photoinduced molecular transformations or phase transitions. Advances in sophisticated technologies and instrumentation in ultrafast science make it now possible to drive ultrafast transformations by stimulating selectively a responsive degree of freedom [1, 2]. In addition, various time-resolved techniques allow for probing selectively the ultrafast and out-of-equilibrium dynamics, the equilibration and the coupling of different degrees of freedom coming into play [3–8]. Directing the functionality of materials towards a desired outcome at the relevant length, time and energy scales is a current challenge in materials' science.

Watching the elementary processes driving the transformation of matter, including electronic and structural dynamics, requires the use of techniques with a temporal resolution approaching the femtosecond range (1 fs = 10^{-15} s) with sub-Ångström spatial resolution. In this way, A. H. Zewail pioneered femtochemistry by developing fs pump–probe spectroscopy to study photochemical processes [9]. Pump–probe techniques use a pump laser pulse to trigger the transformation of molecules or materials and a probe pulse to measure the state of the system at a given time dt after photo-excitation (Figure 1).

The last decades witnessed unprecedented controls of Photo-Induced Phase Transitions (PIPT) [1] through the use of femtosecond (1 fs = 10^{-15} s) UV or visible laser pulses, which excite and reorganize electronic structure and modify the equilibrium atomic coordinates in the crystalline structure. The pumping energy determines the excited degrees of freedom: optical (≈1 eV) photons mainly cause inter-band electronic transitions, whereas mid-IR or THz excitations (≈1–100 meV) can resonantly activate phonon modes. These two kinds of excitations are fundamentally different: the first one promotes the system to an electronically excited state, whereas the second modifies the system within its electronic ground state. Pump–probe experiments spread over a growing community of scientists studying ultrafast phenomena, as new technological developments allow for generating not only ultrashort electromagnetic pulses in the THz, infrared (IR), visible (VIS), ultraviolet (UV) and X-ray range but also pulses of electrons [1, 4, 10–14]. Optical pump–probe spectroscopies, using IR, VIS or UV pulses are home-based experiments that can now routinely operate on a daily basis. However, radiation in the IR–VIS–UV domain does not provide information about the evolution of the atomic structure of matter, except in rare cases of simple systems for which the dependence of potential energy curves on the structural dynamics is known. It was therefore necessary to develop ultra-short pulses of X-ray or electron to perform measurements allowing for watching directly structural dynamics [4, 5, 15–19]. This broad spectrum of techniques allows now for monitoring the temporal evolution of the probed degrees of freedom on their intrinsic timescales, including spin, charge, molecular, lattice and crystalline structure.

Delocalized optical electronic excitation has been studied in hard-condensed matter, with insulators and semi-metals for example. This process modifies the relative electronic population of bonding and anti-bonding bands and the fraction of excited electrons n_e is the control parameter that can continuously reshape the potential energy surface (PES, Figure 2a) because the ultrafast thermalisation of electrons modifies the Fermi-Dirac distribution. This drives collective degrees of freedom of the lattice, such as an optical lattice phonon mode Q_{L}, moving the system over long-range order to a new equilibrium structure. The study of the excitation of the coherent phonon in Bismuth was an important step in the development of ultrafast science [14,20–22]. The crystalline

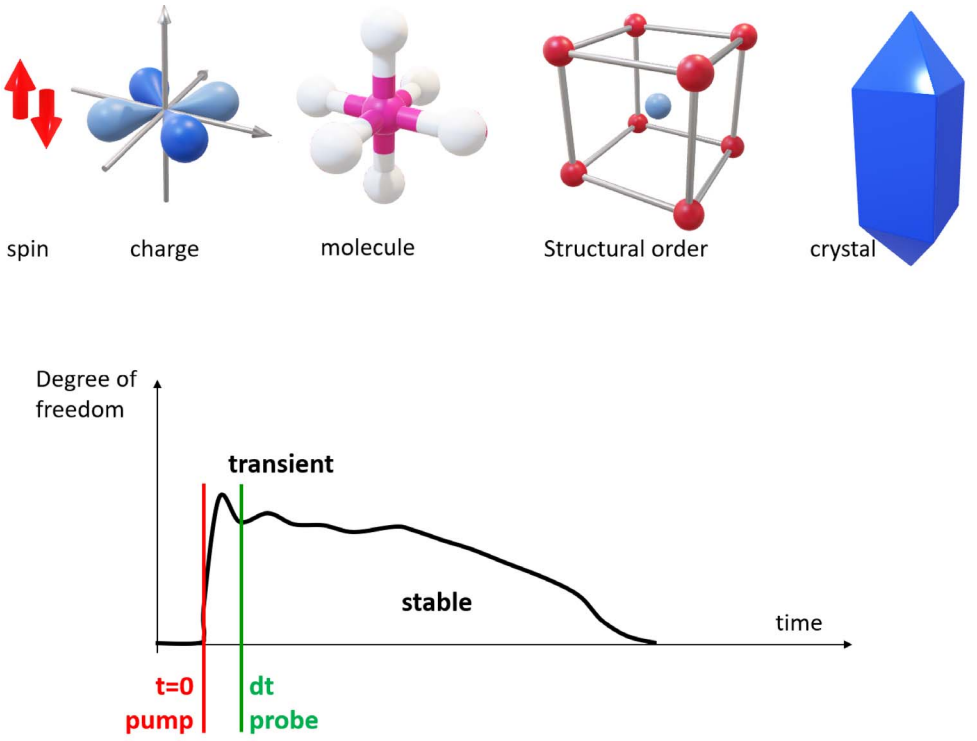


Figure 1. Schematic representation of different degrees of freedom involved in photoinduced processes. Pump–probe techniques allow for monitoring in time the evolution of a degree of freedom.

structure of Bismuth is rhombohedral, with two Bi atoms per unit cell, packed along the large diagonal of the cell with alternating short (X) and long ($1-X$) Bi–Bi interatomic distances. This equilibrium crystalline structure is governed by the electronic population of more or less bonding states (Figure 2a). The optical excitation of Bi populates less bonding electronic states, which modifies the equilibrium distance X. The inter-atomic potential is mainly governed by the thermalization of the electrons, which occurs on a fast timescale. Therefore, after photoexcitation, the potential is changed on a timescale much shorter than the phonon period and the atoms move coherently towards the new equilibrium position. The activation and damping of this coherent phonon Q_L were investigated by various techniques sensitive to the change of electronic state and/or structure [14, 20, 21, 23]. A thermodynamical model based on the two-temperature approach, the one of the electrons and the one of the lattice, evidenced that the coherent atomic motion is and entropy-driven process [24]. In addition, a lattice instability may appear above the critical value $n_e > n_c$ as the PES changes from double to single well, i.e. towards a higher symmetry. However, such processes require a lot of energy: the initial electronic temperature can reach 1000 K. In addition, only a small amount of the optical energy is coherently transferred to Q_L because of energy transfers through electron–phonon and phonon–phonon couplings towards many other degrees of freedom. For some systems, structural reorganization along Q_L can switch physical properties from insulating to metallic state for example [25] and even towards hidden phases [26].

Similar coherent structural dynamics was reported in molecular crystals. The family of $(EDOTTF)_2XF_6$ systems, where X stands for counter anions As, Sb or P, corresponds to 1/4 filled

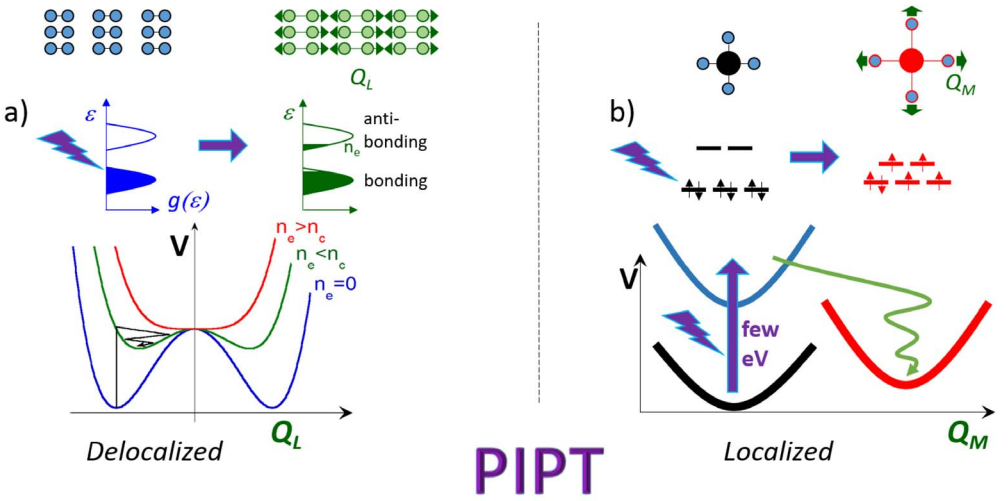


Figure 2. (a) PIPT driven by electronic excitation for delocalized electronic population of antibonding bands modifies the equilibrium of the lattice along Q_L. (b) Electronic excitation localized at the molecular level results in another PES for the new electronic state with different equilibrium structure of the molecule along Q_M.

molecular conductors (in terms of holes), which exhibit charge order in the insulating low temperature phase [27, 28] and the associated symmetry breaking corresponds to a doubling of the unit cell as neutral-bent and ionic-flat $(EDOTTF)_2$ dimers alternate. Those materials display a gigantic response to femtosecond laser excitation in the insulating phase, modulating so optical reflectivity up to 120%. The dynamics is associated with coherent structural reorganization and time-resolved electron diffraction evidenced the molecular motions involved in the process [29]. This is also the case for the molecular crystal $Me_4P[Pt(dmit)_2]_2$ [6], which exhibits a photoinduced charge transfer. Femtosecond electron diffraction studies allowed one to directly observe the coherent molecular motions involved in the process, and clearly identified them as due to a dimer expansion and a librational mode.

PIPTs driven by optical excitation were studied in molecular materials. Some initial processes are local and can be described at the molecular scale. The molecular entity is here the relevant building block: different and discrete PES correspond to discrete molecular electronic states (Figure 2b). The excitation from a ground state (black) to an electronic excited state (blue) may decay and be trapped in a less bonding and metastable state (red) by the structural reorganisation along a molecular mode Q_M. The coupling between electronic excitation and structural reorganizations is also an important aspect responsible for the appearance of light-induced excited spin state trapping (LIESST) in many transition metal complexes with electronic configuration d^4–d^7 and capable of spin crossover [12,30,31]. In these bistable molecular materials, the metal bonded to the ligand (L) may have two spin states in the case of a d^6 configuration: the LS state of electronic configuration ($S = 0$, $t_{2g}^6 e_g^0 L^0$) and the HS state ($S = 2$, $t_{2g}^4 e_g^2 L^0$). The LIESST effect consists in exciting by light a system in the LS state in order to switch it to the HS state. The structural trapping of the photoinduced HS state occurs at the time scale of elementary atomic movements and involves a reorganization of the molecular structure, linked to the variation of the iron-ligand (Fe–L) bond length, which accompanies the population of anti-bonding e_g states. X-ray absorption spectroscopy is a powerful technique for monitoring such local transformation occurring around the metal ion. A recent XANES study performed at the LCLS X-ray free electron laser

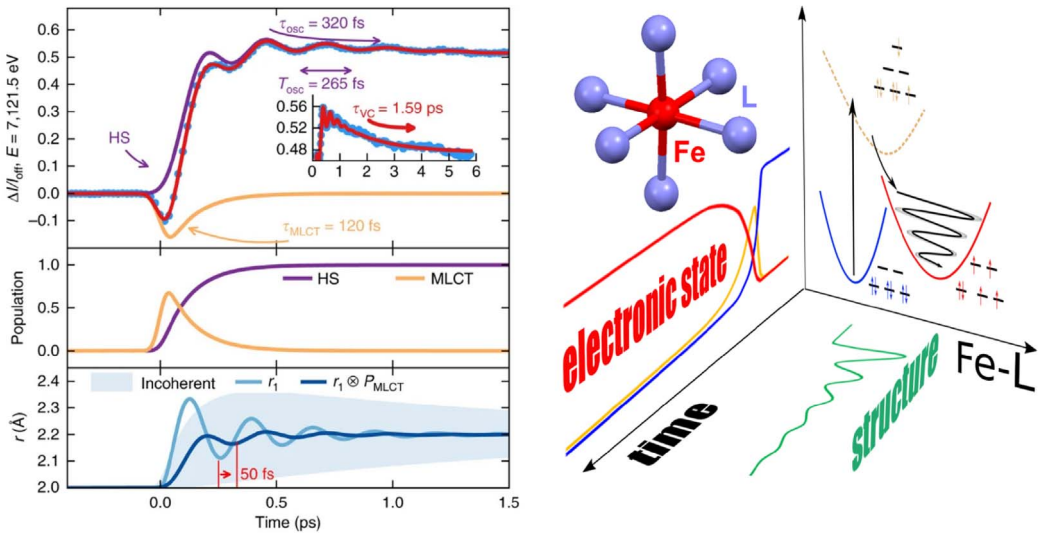


Figure 3. Evolution of the X-ray absorption signal (left) of a spin transition system after fs optical laser excitation, reprinted with permission from [12]. The signal decomposes in terms of electronic state change and structural dynamics with the evolution of the Fe–L distance r (right).

(X-FEL) [12] with a temporal resolution of ~25 fs, made it possible to directly observe the coherent structural dynamics of the ligand during the LIESST effect (Figure 3). XANES also allowed for discriminating the mean change of electronic state and the structural dynamics. The optical excitation $t_{2g} \rightarrow L$ induces a state of metal-ligand charge transfer (MLCT $t_{2g}^5 e_g^0 L^1$), and this change from Fe^{2+} to Fe^{3+} decreases the absorption of X-rays. This state then relaxes towards the HS state via activation and damping of the breathing mode, corresponding to an elongation of the Fe–L bonds, which is characterized by an increase and oscillation of the X-rays absorption. It is then possible to disentangle the electronic and structural dynamics, as shown in Figure 3.

Some molecular systems exhibit intermediate situation, in which the electronic excitation involves several molecules. This is the case for charge-transfer systems undergoing insulator-metal [6] or para- to ferroelectric [32] phase transitions. The past 15 years witnessed development of a broad and expanding spectrum of complementary optical and X-ray techniques, including spectroscopy and diffraction [4]. These techniques have delivered new insights into the dynamics of molecular systems and solids, by investigating how an ultrafast and intense optical pulse drives the transformation process, and how electronic and structural degrees of freedom are coupled, and evolve in real time. For condensed matter, the topics concern a broad variety of mechanisms including coherent structural dynamics [4, 6, 12, 31, 32], cooperative transformation [30], charge-orbital orders [33], etc.

A recent study of a photomagnetic CoFe Prussian blue analogue investigated how coupled charge-transfer and spin transition evolve in time [34]. These systems are coordination networks where cyanide groups connect the Co and the Fe ions in octahedral crystal fields. There are two bistable electronic–structural configurations (Figure 4) linked to a charge transfer (CT) between Fe and Co: the ground $Co^{III}(S = 0)Fe^{II}(S = 0)$ state or the photoinduced $Co^{II}(S = 3/2)Fe^{III}(S = 1/2)$. In the HS $Co^{II}Fe^{III}$ state, the population of anti-binding Co (e_g) orbitals lengthens Co–N bonds by ≈0.2 Å and this spin transition (ST) on the Co is the main reaction coordinate. The photoinduced

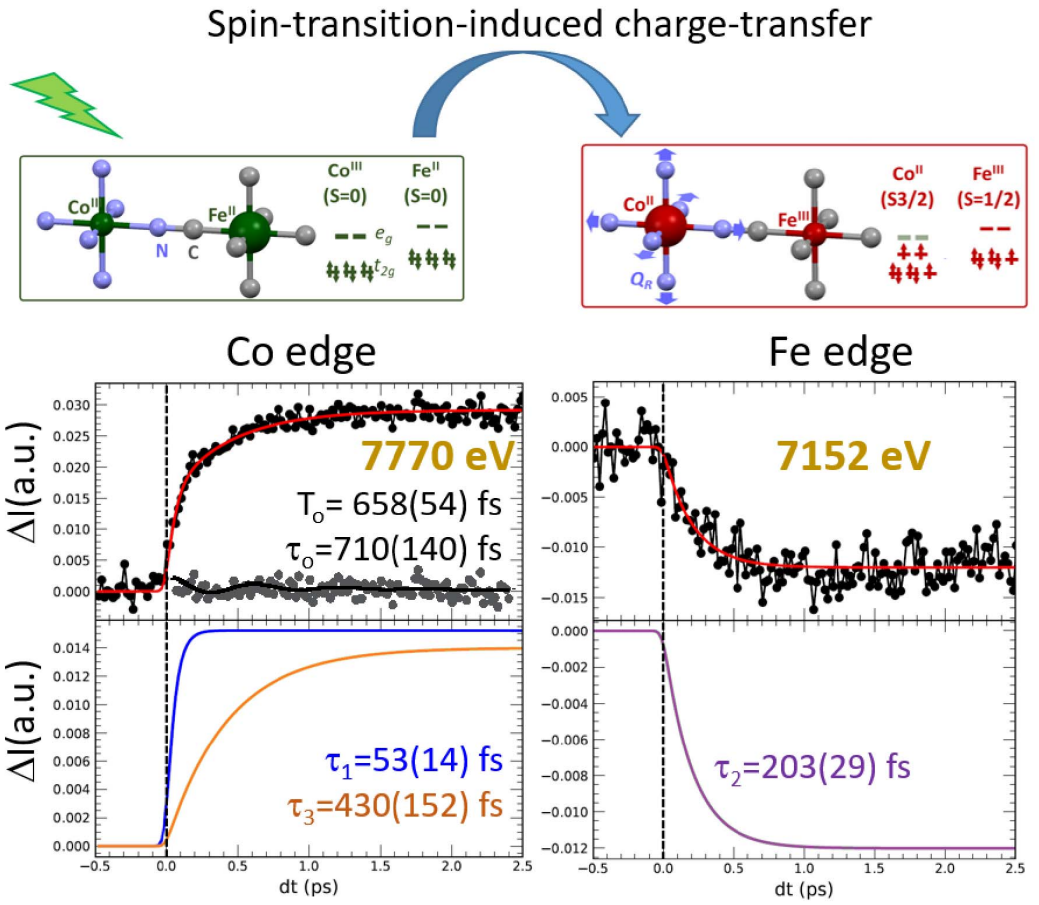


Figure 4. Photomagnetic transition between low and high spin states [34]. XANES spectroscopy measurements show that it is the photoinduced spin transition (ST) around the Co, occurring within ~50 fs as observed at 7770 eV, which induces the charge transfer (CT) within ~200 fs, as observed around the Fe edge (7152 eV), thus following the transformation path STICT.

Fe → Co charge transfer process remained inaccessible and it was then considered that the path followed during the transformation is a photoinduced charge transfer, which induces its turn the spin transition (CTIST transformation lane). The time-resolved XANES measurements performed at the X-FEL LCLS with ≈25 fs time resolution allowed probing selectively the dynamics of electronic and structural degrees of freedom around Fe and Co ions [34]. These results provided a direct insight into electronic and structural dynamics: the Co^{III} (t_{2g}) → Co^{III} (e_g) optical excitation induces the spin transition on Co and elongates the Co–N bonds within ≈50 fs, as characterized by a rapid variation in absorption above the threshold Co (7770 eV, Figure 4). XANES, which is a technique of choice for measuring changes in the oxidation state of metals, revealed that the Fe → Co (CT) charge transfer takes place in a second step within ≈200 fs, as characterized by the spectral shift at the Fe absorption edge (7152 eV). These results provide a clear answer to a question debated for decades, by demonstrating that in this photoexcited prototype CoFe compound, the transformation pathway is a photoactivated spin transition, which induces charge transfer (STICT in Figure 4).

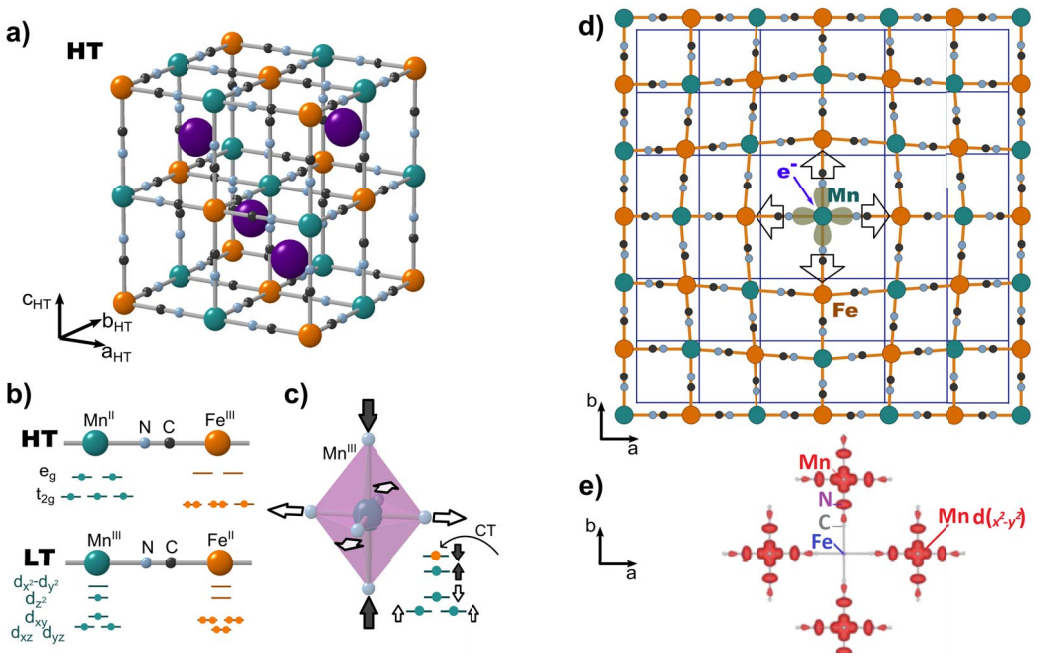


Figure 5. (a) Crystalline structure of RbMnFe PBA in the cubic HT phase. (b) Schematic valence states and electronic configurations in the LT $Mn^{III}Fe^{II}$ and HT $Mn^{II}Fe^{III}$ phases. (c) The $Mn^{III}Fe^{II} \rightarrow Mn^{II}Fe^{III}$ charge transfer, populating the antibonding Mn $d(x^2 - y^2)$ state, is stabilized by the reverse Jahn–Teller distortion elongating Mn–N bonds along a and b and shrinking the ones along c. (d) Schematic representation of the lattice expansion in the (a, b) plane distortion due to the CT small-polaron. (e) The CT populates the Mn $d(x^2 - y^2)$ state and is self-trapped by Mn–N bond elongation. Reprinted with permission from [35].

$RbMn[Fe(CN)_6]$ Prussian blue analogues also exhibit diverse CT-based functionalities [36–38]. The additional complexity comes the fact that the bistability between the high-temperature cubic (HT) $Mn^{II}(S = 5/2)Fe^{III}(S = 1/2)$ state and the low-temperature (LT) $Mn^{III}(S = 2)Fe^{II}(S = 0)$ state is also coupled to a symmetry breaking towards a tetragonal lattice, due to Jahn–Teller distortion around the Mn^{III} [39, 40]. Since CT couples to Jahn–Teller distortion, the nature of the photoinduced process was questioned: is it a Jahn–Teller-induced CT or a CT-induced structural trapping? Femtosecond optical pump–probe spectroscopy revealed that two photoswitching pathways exist, depending on the excitation pump wavelength, which is confirmed by band structure calculations [41]. Photoexcitation of α spins corresponds to the Mn(d–d) band, which drives reverse Jahn–Teller distortion through the population of antibonding Mn–N orbitals, and induces CT within ~190 fs. Photoexcitation of β spins drives intervalence Fe → Mn CT towards non-bonding states and results in a slower dynamic. Time resolved X-ray diffraction studies also revealed the anisotropic out-of-equilibrium lattice dynamics triggered by the self-trapping of photo-induced $Mn^{III}Fe^{II} \rightarrow Mn^{II}Fe^{III}$ CT [35]. The observed dynamics evidenced a decoupling in time of the lattice expansion and the ferroelastic Jahn–Teller distortion. The anisotropic out-of-equilibrium lattice dynamics is triggered by the self-trapping of photo-induced $Mn^{III}Fe^{II} \rightarrow Mn^{II}Fe^{III}CT$. The impulsive lattice response is driven by the local Jahn–Teller reorganization, which elongates the a and b lattice parameters and shrinks the c axis (Figure 5). The structural reorganization is stabilized by a displacive volume expansion, controlled by the long-lived

photo-induced CT small-polarons. Indeed, CT populates the lowest unoccupied crystalline orbital, with electronic density highly localized on antibonding Mn($d_{x^2-y^2}$) and N orbitals. This change of electronic state elongates Mn–N bonds in the (a, b) lattice plane and is therefore responsible for the anisotropic volume expansion.

Photoinduced phenomena are often multi-scale processes. The recent study by Mariette *et al.* [36], based on femtosecond X-ray diffraction experiments, revealed how electronic and structural precursor phenomena generate strain waves and coherent macroscopic transformation pathway for the semiconducting-to-metal transition in bistable Ti_3O_5 nanocrystals [42]. The authors have measured the lattice deformation in the photoinduced phase transition as a function of time, and monitored the intra-cell distortions around the light absorbing metal dimer and the long-range deformations governed by acoustic waves. The photoinduced phase propagates from the laser-exposed surface.

The scale of energy involved in optical excitation is the limiting factor in many of the previous studies. The energy difference between the starting and the final phases in bistable systems for instance is of the order of thermal energy ($k_B T < 30$ meV at $T = 300$ K), which is much lower than the energy of optical photons (eV) [1]. PIPTs driven by optical excitation are then often dominated by heat dissipation, which hinders establishment of ordered state or destroys the coherent dynamics. Temperature rise inevitably favors states of higher entropy and higher symmetry. Since emergence of functions like ferro-electricity is related to symmetry breaking, and hence to lower entropy states, a new suitable control method is required. By acting on lattice vibration modes at a resonant and relevant energy scale (10–250 meV), the nonlinear phononics (NLP) is a potential candidate method for tuning materials along a transformation pathway while allowing to circumvent the above-mentioned limitations (Figure 6). It preserves all advantages intrinsic to the ultrafast time-scales while alleviating the shortcomings of electronic excitations, whereby electron–phonon couplings are not controlled, and selectively activates a highly responsive phonon mode. NLP is based on a strong and resonant excitation of low-energy IR phonon Q_{IR} (frequency Ω_{IR}) by high-power femtosecond mid-IR lasers (1000 s·cm^{-1}). A. Cavalleri's group demonstrated that NLP can favors superconductivity or drive insulator-metal transition [43–48]. According to the theory of nonlinear phononics developed by Subedi and Georges [43, 49] the intense laser field $F(t)$ of the IR pulse populates a significant quanta of Q_{IR} phonons ($n \gg 1$) with large amplitude $\langle Q_{IR}^2 \rangle$. The non-linear coupling to a phonon mode Q_{TS} moves its equilibrium position by $\propto F^2(\Omega_{IR}/\Omega_{TS})^2$. NLP allows then to tune the potential V_{TS} along a transformation pathway, towards another phase of different structural-electronic orders. Some recent uses of NLP via mid-IR phonon excitations in hard condensed matter include large perturbations of orbital [50], magnetic [51–53] and ferroelectric [54] orders. Hence, NLP promises capabilities insofar unachieved in PIPT, as the ultrafast modification of the potential, occurring on a few Q_{IR} phonon periods, will drive coherent and collective transformations.

The field of ultrafast phenomena in condensed matter is rapidly expending, with a large variety of topics and techniques, and this special issue perfectly illustrates this diversity. Recent advances allowing monitoring ultrafast phenomena are presented by Chong-Yu Ruan *et al.* for ultrafast electron diffraction and Michael Wulff *et al.* for X-ray techniques at synchrotron and X-FEL. Yoichi Okimoto *et al.* show how time-resolved Raman spectroscopy can be used to study the picosecond dynamics of the photo-excited charge-ordered perovskite-type cobalt oxides. Marino Marsi *et al.* present time-resolved Angle Resolved Photoemission Spectroscopy ARPES, which allows for visualizing directly on the femtosecond time scale the evolution of band dispersion of photoexcited solids. Stefan Haacke *et al.* revisit with optical spectroscopy the sub-picosecond photo-isomerization process. Claire Laulhé *et al.* use X-ray diffraction to investigate to ultrafast photoinduced dynamics of an incommensurate charge density wave in 1T–TaS_2. Alaska Subedi is reviewing the emerging field of non-linear phononics and its underlying theory.

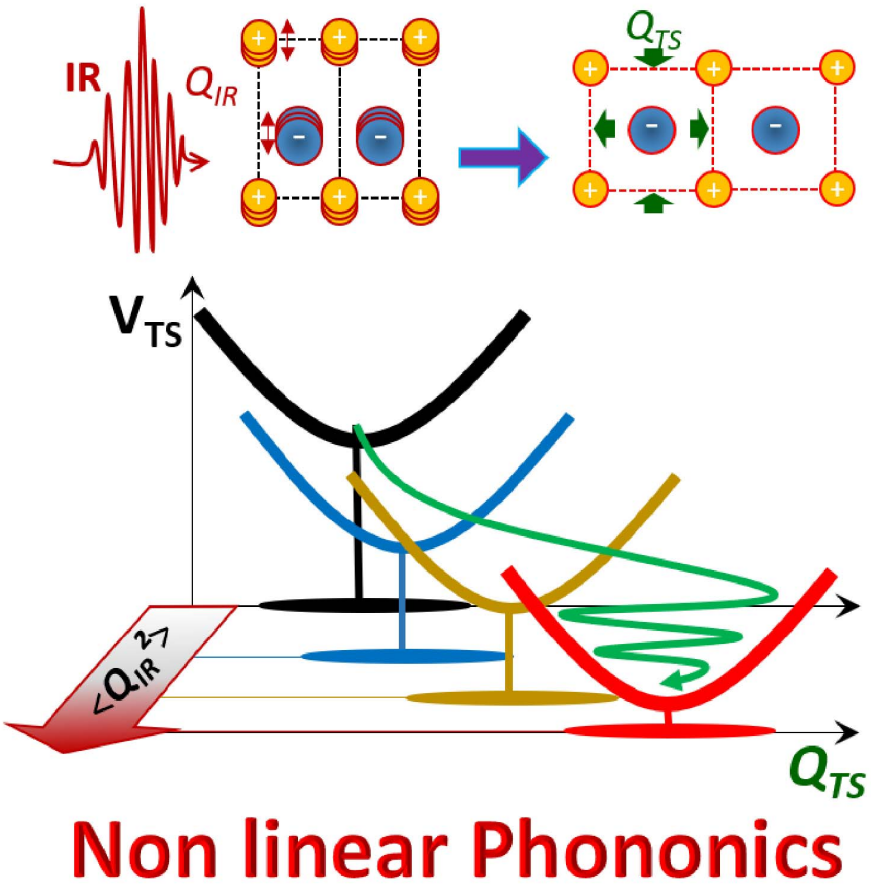


Figure 6. Nonlinear phononics drives transformation in the electronic ground state: a highly excited $\langle Q_{\mathrm{IR}}^2 \rangle$ anharmonically couples to a totally symmetric mode Q_{TS}, rectifies its potential V_{TS} and drives a structural reorganisation by modifying the equilibrium position of Q_{TS}.

References

[1] D. N. Basov, R. D. Averitt, D. Hsieh, "Towards properties on demand in quantum materials", *Nat. Mater.* **16** (2017), p. 1077-1088.

[2] K. Nasu, *Photoinduced Phase Transitions*, World Scientific, Singapore, Hackensack, NJ, 2004.

[3] A. H. Zewail, "Chemistry at the uncertainty limit", *Angew. Chem. Int. Ed.* **40** (2001), p. 4371-4375.

[4] M. Chergui, E. Collet, "Photoinduced structural dynamics of molecular systems mapped by time-resolved X-ray methods", *Chem. Rev.* **117** (2017), p. 11025-11065.

[5] E. Collet, "Dynamical structural science", *Acta Crystallogr. A* **66** (2010), p. 133-134.

[6] T. Ishikawa, S. A. Hayes, S. Keskin, G. Corthey, M. Hada, K. Pichugin, A. Marx, J. Hirscht, K. Shionuma, K. Onda, Y. Okimoto, S.-y. Koshihara, T. Yamamoto, H. Cui, M. Nomura, Y. Oshima, M. Abdel-Jawad, R. Kato, R. J. D. Miller, "Direct observation of collective modes coupled to molecular orbital–driven charge transfer", *Science* **350** (2015), p. 1501-1505.

[7] F. Schmitt, P. S. Kirchmann, U. Bovensiepen, R. G. Moore, L. Rettig, M. Krenz, J. H. Chu, N. Ru, L. Perfetti, D. H. Lu, M. Wolf, I. R. Fisher, Z. X. Shen, "Transient electronic structure and melting of a charge density wave in $TbTe_3$", *Science* **321** (2008), p. 1649-1652.

[8] C. Boeglin, E. Beaurepaire, V. Halte, V. Lopez-Flores, C. Stamm, N. Pontius, H. A. Durr, J. Y. Bigot, "Distinguishing the ultrafast dynamics of spin and orbital moments in solids", *Nature* **465** (2010), p. 458-461.

[9] A. H. Zewail, F. C. d. Schryver, S. D. Feyter, G. Schweitzer, *Femtochemistry: with the Nobel Lecture of A. Zewail*, Wiley-VCH, Weinheim New York, 2001.

[10] T. Kampfrath, K. Tanaka, K. A. Nelson, "Resonant and nonresonant control over matter and light by intense terahertz transients", *Nat. Photonics* **7** (2013), p. 680-690.

[11] K. Zhang, R. Ash, G. S. Girolami, J. Vura-Weis, "Tracking the Metal-centered triplet in photoinduced spin crossover of $Fe(phen)_3^{(2+)}$ with tabletop femtosecond M-Edge X-ray absorption near-edge structure spectroscopy", *J. Am. Chem. Soc.* **141** (2019), no. 43, p. 17180-17188.

[12] H. T. Lemke, K. S. Kjær, R. Hartsock, T. Brandt van Driel, M. Chollet, J. M. Glownia, S. Song, D. Zhu, E. Pace, S. F. Matar, M. N. Nielsen, M. Benfatto, K. J. Gaffney, E. Collet, M. Cammarata, "Coherent structural trapping through wave packet dispersion during photoinduced spin state switching", *Nat. Commun.* **8** (2017), article no. 15342.

[13] S. Zerdane, L. Wilbraham, M. Cammarata, O. Iasco, E. Rivière, M. L. Boillot, I. Ciofini, E. Collet, "Comparison of structural dynamics and coherence of d–d and MLCT light-induced spin state trapping", *Chem. Sci.* **8** (2017), p. 4978-4986.

[14] J. Faure, J. Mauchain, E. Papalazarou, M. Marsi, D. Boschetto, I. Timrov, N. Vast, Y. Ohtsubo, B. Arnaud, L. Perfetti, "Direct observation of electron thermalization and electron-phonon coupling in photoexcited bismuth", *Phys. Rev. B* **88** (2013), article no. 075120.

[15] M. Chergui, A. H. Zewail, "Electron and X-ray methods of ultrafast structural dynamics: advances and applications", *Chemphyschem* **10** (2009), p. 28-43.

[16] T. Graber, S. Anderson, H. Brewer, Y. S. Chen, H. S. Cho, N. Dashdorj, R. W. Henning, I. Kosheleva, G. Macha, M. Meron, R. Pahl, Z. Ren, S. Ruan, F. Schotte, V. Srajer, P. J. Viccaro, F. Westferro, P. Anfinrud, K. Moffat, "BioCARS: a synchrotron resource for time-resolved X-ray science", *J. Synchrotron Radiat.* **18** (2011), p. 658-670.

[17] Y. Jiang, L. C. Liu, H. M. Müller-Werkmeister, C. Lu, D. Zhang, R. L. Field, A. Sarracini, G. Moriena, E. Collet, R. J. D. Miller, "Structural dynamics upon photoexcitation in a spin crossover crystal probed with femtosecond electron diffraction", *Angew. Chem. Int. Ed.* **56** (2017), p. 7130-7134.

[18] L. X. Chen, X. Zhang, M. L. Shelby, "Recent advances on ultrafast X-ray spectroscopy in the chemical sciences", *Chem. Sci.* **5** (2014), p. 4136-4152.

[19] M. Cammarata, L. Eybert, F. Ewald, W. Reichenbach, M. Wulff, P. Anfinrud, F. Schotte, A. Plech, Q. Kong, M. Lorenc, B. Lindenau, J. Rabiger, S. Polachowski, "Chopper system for time resolved experiments with synchrotron radiation", *Rev. Sci. Instrum.* **80** (2009), article no. 015101.

[20] K. Sokolowski-Tinten, C. Blome, J. Blums, A. Cavalleri, C. Dietrich, A. Tarasevitch, I. Uschmann, E. Forster, M. Kammler, M. Horn-von Hoegen, D. von der Linde, "Femtosecond X-ray measurement of coherent lattice vibrations near the Lindemann stability limit", *Nature* **422** (2003), p. 287-289.

[21] D. M. Fritz, D. A. Reis, B. Adams, R. A. Akre, J. Arthur, C. Blome, P. H. Bucksbaum, A. L. Cavalieri, S. Engemann, S. Fahy, R. W. Falcone, P. H. Fuoss, K. J. Gaffney, M. J. George, J. Hajdu, M. P. Hertlein, P. B. Hillyard, M. H. V. Hoegen, M. Kammler, J. Kaspar, R. Kienberger, P. Krejcik, S. H. Lee, A. M. Lindenberg, B. McFarland, D. Meyer, T. Montagne, E. D. Murray, A. J. Nelson, M. Nicoul, R. Pahl, J. Rudati, H. Schlarb, D. P. Siddons, K. Sokolowski-Tinten, T. Tschentscher, D. von der Linde, J. B. Hastings, "Ultrafast bond softening in bismuth: Mapping a solid's interatomic potential with X-rays", *Science* **315** (2007), p. 633-636.

[22] S. L. Johnson, P. Beaud, E. Vorobeva, C. J. Milne, E. D. Murray, S. Fahy, G. Ingold, "Non-equilibrium phonon dynamics studied by grazing-incidence femtosecond X-ray crystallography", *Acta Crystallogr. A* **66** (2010), p. 157-167.

[23] T. Garl, E. G. Gamaly, D. Boschetto, A. V. Rode, B. Luther-Davies, A. Rousse, "Birth and decay of coherent optical phonons in femtosecond-laser-excited bismuth", *Phys. Rev. B* **78** (2008), article no. 134302.

[24] Y. Giret, A. Gellé, B. Arnaud, "Entropy driven atomic motion in laser-excited bismuth", *Phys. Rev. Lett.* **106** (2011), article no. 155503.

[25] A. Cavalleri, C. Toth, C. W. Siders, J. A. Squier, F. Raksi, P. Forget, J. C. Kieffer, "Femtosecond structural dynamics in VO_2 during an ultrafast solid-solid phase transition", *Phys. Rev. Lett.* **8723** (2001), article no. 237401.

[26] H. Ichikawa, S. Nozawa, T. Sato, A. Tomita, K. Ichiyanagi, M. Chollet, L. Guerin, N. Dean, A. Cavalleri, S.-i. Adachi, T.-h. Arima, H. Sawa, Y. Ogimoto, M. Nakamura, R. Tamaki, K. Miyano, S.-y. Koshihara, "Transient photoinduced "hidden" phase in a manganite", *Nat. Mater.* **10** (2011), p. 101-105.

[27] M. Chollet, L. Guerin, N. Uchida, S. Fukaya, H. Shimoda, T. Ishikawa, K. Matsuda, T. Hasegawa, A. Ota, H. Yamochi, G. Saito, R. Tazaki, S.-i. Adachi, S.-y. Koshihara, "Gigantic Photoresponse in $\frac{1}{4}$-Filled-Band Organic Salt $(EDO\text{-}TTF)_2PF_6$", *Science* **307** (2005), p. 86-89.

[28] M. Servol, N. Moisan, E. Collet, H. Cailleau, W. Kaszub, L. Toupet, D. Boschetto, T. Ishikawa, A. Moréac, S. Koshihara, M. Maesato, M. Uruichi, X. Shao, Y. Nakano, H. Yamochi, G. Saito, M. Lorenc, "Local response to light excitation in the charge-ordered phase of$(EDO\text{-}TTF)_2SbF_6$", *Phys. Rev. B* **92** (2015), article no. 024304.

[29] M. Gao, C. Lu, H. Jean-Ruel, L. C. Liu, A. Marx, K. Onda, S. Y. Koshihara, Y. Nakano, X. Shao, T. Hiramatsu, G. Saito, H. Yamochi, R. R. Cooney, G. Moriena, G. Sciaini, R. J. Miller, "Mapping molecular motions leading to charge delocalization with ultrabright electrons", *Nature* **496** (2013), p. 343-346.

[30] R. Bertoni, M. Lorenc, H. Cailleau, A. Tissot, J. Laisney, M. L. Boillot, L. Stoleriu, A. Stancu, C. Enachescu, E. Collet,

"Elastically driven cooperative response of a molecular material impacted by a laser pulse", *Nat. Mater.* **15** (2016), p. 606-610.

[31] M. Cammarata, R. Bertoni, M. Lorenc, H. Cailleau, S. Di Matteo, C. Mauriac, S. F. Matar, H. Lemke, M. Chollet, S. Ravy, C. Laulhe, J. F. Letard, E. Collet, "Sequential activation of molecular breathing and bending during spin-crossover photoswitching revealed by femtosecond optical and X-ray absorption spectroscopy", *Phys. Rev. Lett.* **113** (2014), article no. 227402.

[32] E. Collet, M. H. Lemee-Cailleau, M. Buron-Le Cointe, H. Cailleau, M. Wulff, T. Luty, S. Y. Koshihara, M. Meyer, L. Toupet, P. Rabiller, S. Techert, "Laser-induced ferroelectric structural order in an organic charge-transfer crystal", *Science* **300** (2003), p. 612-615.

[33] P. Beaud, A. Caviezel, S. O. Mariager, L. Rettig, G. Ingold, C. Dornes, S. W. Huang, J. A. Johnson, M. Radovic, T. Huber, T. Kubacka, A. Ferrer, H. T. Lemke, M. Chollet, D. Zhu, J. M. Glownia, M. Sikorski, A. Robert, H. Wadati, M. Nakamura, M. Kawasaki, Y. Tokura, S. L. Johnson, U. Staub, "A time-dependent order parameter for ultrafast photoinduced phase transitions", *Nat. Mater.* **13** (2014), p. 923-927.

[34] M. Cammarata, S. Zerdane, L. Balducci, G. Azzolina, S. Mazerat, C. Exertier, M. Trabuco, M. Levantino, R. Alonso-Mori, J. Glownia, S. Song, L. Catala, T. Mallah, S. F. Matar, E. Collet, "Charge transfer driven by ultrafast spin transition in a CoFe Prussian blue analogue", *Nat. Chem.* **13** (2021), p. 10-14.

[35] G. Azzolina, R. Bertoni, C. Mariette, M. Cammarata, E. Trzop, C. Ecolivet, M. Sander, M. Levantino, H. Tokoro, K. Imoto, M. Yoshikiyo, S. Ohkoshi, E. Collet, "Out-of-equilibrium lattice response to photo-induced charge-transfer in a MnFe Prussian blue analogue", *J. Mater. Chem. C* **9** (2021), p. 6773-6780.

[36] H. Tokoro, S. Ohkoshi, "Multifunctional Material: Bistable Metal–Cyanide Polymer of Rubidium Manganese Hexacyanoferrate", *Bull. Chem. Soc. Jpn.* **88** (2015), p. 227-239.

[37] K. Kato, Y. Moritomo, M. Takata, M. Sakata, M. Umekawa, N. Hamada, S. Ohkoshi, H. Tokoro, K. Hashimoto, "Direct observation of charge transfer in double-perovskite-like $RbMnFe(CN)_6$", *Phys. Rev. Lett.* **91** (2003), article no. 255502.

[38] S. Ohkoshi, H. Tokoro, M. Utsunomiya, M. Mizuno, M. Abe, K. Hashimoto, "Observation of spin transition in an octahedrally Coordinated Manganese(II) compound", *J. Phys. Chem. B* **106** (2002), p. 2423-2425.

[39] H. Tokoro, S. Ohkoshi, T. Matsuda, K. Hashimoto, "A large thermal hysteresis loop produced by a charge-transfer phase transition in a rubidium manganese hexacyanoferrate", *Inorg. Chem.* **43** (2004), p. 5231-5236.

[40] G. Azzolina, R. Bertoni, C. Ecolivet, H. Tokoro, S. Ohkoshi, E. Collet, "Landau theory for non-symmetry-breaking electronic instability coupled to symmetry-breaking order parameter applied to Prussian blue analog", *Phys. Rev. B* **102** (2020), article no. 134104.

[41] G. Azzolina, H. Tokoro, K. Imoto, M. Yoshikiyo, S.-i. Ohkoshi, E. Collet, "Exploring ultrafast photoswitching pathways in RbMnFe Prussian Blue Analogue", *Angew. Chem. Int. Ed.* (2021).

[42] C. Mariette, M. Lorenc, H. Cailleau, E. Collet, L. Guérin, A. Volte, E. Trzop, R. Bertoni, X. Dong, B. Lépine, O. Hernandez, E. Janod, L. Cario, V. Ta Phuoc, S. Ohkoshi, H. Tokoro, L. Patthey, A. Babic, I. Usov, D. Ozerov, L. Sala, S. Ebner, P. Böhler, A. Keller, A. Oggenfuss, T. Zmofing, S. Redford, S. Vetter, R. Follath, P. Juranic, A. Schreiber, P. Beaud, V. Esposito, Y. Deng, G. Ingold, M. Chergui, G. F. Mancini, R. Mankowsky, C. Svetina, S. Zerdane, A. Mozzanica, A. Bosak, M. Wulff, M. Levantino, H. Lemke, M. Cammarata, "Strain wave pathway to semiconductor-to-metal transition revealed by time-resolved X-ray powder diffraction", *Nat. Commun.* **12** (2021), article no. 1239.

[43] A. Subedi, A. Cavalleri, A. Georges, "Theory of nonlinear phononics for coherent light control of solids", *Phys. Rev. B* **89** (2014), article no. 220301.

[44] D. Nicoletti, A. Cavalleri, "Nonlinear light–matter interaction at terahertz frequencies", *Adv. Opt. Photonics* **8** (2016), p. 401-464.

[45] M. Forst, C. Manzoni, S. Kaiser, Y. Tomioka, Y. Tokura, R. Merlin, A. Cavalleri, "Nonlinear phononics as an ultrafast route to lattice control", *Nat. Phys.* **7** (2011), p. 854-856.

[46] J. Zhang, R. D. Averitt, "Dynamics and control in complex transition metal oxides", *Annu. Rev. Mater. Res.* **44** (2014), p. 19-43.

[47] R. Mankowsky, A. Subedi, M. Forst, S. O. Mariager, M. Chollet, H. T. Lemke, J. S. Robinson, J. M. Glownia, M. P. Minitti, A. Frano, M. Fechner, N. A. Spaldin, T. Loew, B. Keimer, A. Georges, A. Cavalleri, "Nonlinear lattice dynamics as a basis for enhanced superconductivity in $YBa_2Cu_3O_{6.5}$", *Nature* **516** (2014), p. 71-73.

[48] M. Liu, H. Y. Hwang, H. Tao, A. C. Strikwerda, K. Fan, G. R. Keiser, A. J. Sternbach, K. G. West, S. Kittiwatanakul, J. Lu, S. A. Wolf, F. G. Omenetto, X. Zhang, K. A. Nelson, R. D. Averitt, "Terahertz-field-induced insulator-to-metal transition in vanadium dioxide metamaterial", *Nature* **487** (2012), p. 345-348.

[49] A. Subedi, "Midinfrared-light-induced ferroelectricity in oxide paraelectrics via nonlinear phononics", *Phys. Rev. B* **95** (2017), article no. 134113.

[50] R. I. Tobey, D. Prabhakaran, A. T. Boothroyd, A. Cavalleri, "Ultrafast electronic phase transition in $La_{1/2}Sr_{3/2}MnO_4$ by coherent vibrational excitation: evidence for nonthermal melting of orbital order", *Phys. Rev. Lett.* **101** (2008), article no. 197404.

[51] M. Först, R. I. Tobey, S. Wall, H. Bromberger, V. Khanna, A. L. Cavalieri, Y. D. Chuang, W. S. Lee, R. Moore, W. F.

Schlotter, J. J. Turner, O. Krupin, M. Trigo, H. Zheng, J. F. Mitchell, S. S. Dhesi, J. P. Hill, A. Cavalleri, "Driving magnetic order in a manganite by ultrafast lattice excitation", *Phys. Rev. B* **84** (2011), article no. 241104.

[52] M. Forst, A. D. Caviglia, R. Scherwitzl, R. Mankowsky, P. Zubko, V. Khanna, H. Bromberger, S. B. Wilkins, Y. D. Chuang, W. S. Lee, W. F. Schlotter, J. J. Turner, G. L. Dakovski, M. P. Minitti, J. Robinson, S. R. Clark, D. Jaksch, J. M. Triscone, J. P. Hill, S. S. Dhesi, A. Cavalleri, "Spatially resolved ultrafast magnetic dynamics initiated at a complex oxide heterointerface", *Nat. Mater.* **14** (2015), p. 883-888.

[53] T. F. Nova, A. Cartella, A. Cantaluppi, M. Först, D. Bossini, R. V. Mikhaylovskiy, A. V. Kimel, R. Merlin, A. Cavalleri, "An effective magnetic field from optically driven phonons", *Nat. Phys.* **13** (2017), p. 132-136.

[54] R. Mankowsky, A. von Hoegen, M. Forst, A. Cavalleri, "Ultrafast reversal of the ferroelectric polarization", *Phys. Rev. Lett.* **118** (2017), article no. 197601.