Ultrafast energy- and momentum-resolved dynamics of magnetic correlations in the photo-doped Mott insulator Sr$_2$IrO$_4$

M. P. M. Dean$^{1, *}$, Y. Cao$^{1, *}$, X. Liu$^{2, 3, *}$, S. Wall$^{4}$, D. Zhu$^{5}$, R. Mankowsky$^{6, 7}$, V. Thampy$^{1}$, X. M. Chen$^{1}$, J. G. Vale$^{8}$, D. Casa$^{9}$, Jungho Kim$^{6}$, A. H. Said$^{9}$, P. Juhas$^{1}$, R. Alonso-Mori$^{10}$, J. M. Glownia$^{5}$, A. Robert$^{5}$, J. Robinson$^{5}$, M. Sikorski$^{5}$, S. Song$^{5}$, M. Kozina$^{8}$, H. Lemke$^{5}$, L. Patthey$^{10}$, S. Owada$^{11}$, T. Katayama$^{12}$, M. Yabashi$^{11}$, Yoshikazu Tanaka$^{11}$, T. Togashi$^{12}$, J. Liu$^{13}$, C. Rayan Serraio$^{14}$, B. J. Kim$^{15}$, L. Huber$^{16}$, C.-L. Chang$^{17}$, D. F. McMorrow$^{8}$, M. Först$^{6, 7}$ and J. P. Hill$^{1}$

Measuring how the magnetic correlations evolve in doped Mott insulators has greatly improved our understanding of the pseudogap, non-Fermi liquids and high-temperature superconductivity$^{1–4}$. Recently, photo-excitation has been used to induce similarly exotic states transiently$^{6–7}$. However, the lack of available probes of magnetic correlations in the time domain hinders our understanding of these photo-induced states and how they could be controlled. Here, we implement magnetic resonant inelastic X-ray scattering at a free-electron laser to directly determine the magnetic dynamics after photo-doping the Mott insulator Sr$_2$IrO$_4$. We find that the non-equilibrium state, 2 ps after the excitation, exhibits strongly suppressed long-range magnetic order, but hosts photo-carriers that induce strong, non-thermal magnetic correlations. These two-dimensional (2D) in-plane Néel correlations recover within a few picoseconds, whereas the three-dimensional (3D) long-range magnetic order restores on a fluence-dependent timescale of a few hundred picoseconds. The marked difference in these two timescales implies that the dimensionality of magnetic correlations is vital for our understanding of ultrafast magnetic dynamics.

In the layered perovskite Sr$_2$IrO$_4$, multiple interactions conspire to determine its electronic configuration. Strong spin–orbit coupling splits the Ir 5d states to form a narrow electronic band that can be further split by the modest on-site Coulomb repulsion to generate an antiferromagnetic Mott insulating state with close structural and electronic analogies to the superconducting cuprates$^{2, 3}$.$^{8–9}$. It has been well established that when a perturbation destroys magnetic order in a Mott insulator, the resulting new state frequently exhibits unusual properties$^{10}$. For example, surface doping and Rh–Ir substitution in Sr$_2$IrO$_4$ have generated novel Fermi-arc and pseudogap behaviour$^{11–12}$, and some have argued that doped Sr$_2$IrO$_4$ might host high-temperature superconductivity$^{13}$. In both cases, magnetic correlations were argued to play a critical role in the formation of these states. Photo-doping a Mott insulator using ultrafast lasers provides an alternative route to create transient versions of these exotic states, with the advantage that the resulting states are tunable and reversible. So far, however, there has been a lack of appropriate tools to probe the momentum and energy dependence of the electronic and magnetic correlations characterizing these ultrafast transient states.

Figure 1 illustrates our experimental approach. Sr$_2$IrO$_4$ was cooled to 110 K, well below its Néel ordering temperature of 240 K (ref. 13). Pump laser pulses with an energy of 620 meV (2 μm) drive carriers from the lower Hubbard band to the upper Hubbard band$^{14}$. The transient magnetic response to this pump was characterized using a free-electron laser. X-ray photons were tuned to the Ir L$_3$ resonance to couple to the spin degree of freedom through the resonant magnetic X-ray scattering mechanism and photons scattered around 90° were measured as a function of momentum transfer, Q, energy loss, E, and time delay, t. Further details are provided in the Methods.

Figure 2a,b plots the time and fluence dependence of the (−3, −2, 28) magnetic Bragg peak intensity in Sr$_2$IrO$_4$, which is sensitive to the presence of 3D magnetic order. This intensity is measured by an area detector without energy analysis of the scattered photons. We find that fluences of $\geq 5$ mJ cm$^{-2}$ destroy the 3D magnetic order based on the criterion of having $\leq 10\%$ remnant...
X-ray pulses from a free-electron laser (shown in purple) probe the resulting transient state. The RIXS planes plot simple spin-wave calculations based on an increased thermal population of magnons after the pulse.

The incident X-ray pulses excite an Ir $2p$ core electron into the $5d$ valence band, to couple to the spin degree of freedom. The resulting emitted photon encodes the magnetic and orbital configuration of the transient state$^{23}$. 

**Figure 1** | Experimental configuration. 

- **a.** The scattering set-up. The vertically polarized pump pulse (shown in red) is incident on the $ab$-face of Sr$_2$IrO$_4$. X-ray pulses from a free-electron laser (shown in purple) probe the resulting transient state. X-rays that are scattered close to 90° are either directly measured, to access the magnetic Bragg peak that probes the presence or absence of 3D magnetic order, or energy analysed to access the inelastic spectrum, which is particularly sensitive to the 2D magnetic correlations. The basic in-plane structural unit of Sr$_2$IrO$_4$ is outlined with a dotted black line. 
- **b.** An illustration of the pump and probe processes. The 620 meV (2 µm) pump beam (in red) photo-dopes the sample, exciting an electron across the Fermi energy, $E_F$, from the lower Hubbard band (LHB) to the upper Hubbard band (UHB). Horizontally polarized 11.215 keV X-ray pulses from a free-electron laser (shown in purple) probe the resulting transient state. The incident X-ray pulses excite an Ir $2p$ core electron into the $5d$ valence band, to couple to the spin degree of freedom. The resulting emitted photon encodes the magnetic and orbital configuration of the transient state$^{23}$. 
- **c.** Illustration of the detection of X-rays as a function of energy loss, momentum transfer and time delay, encoding the time-dependent magnetic correlations in the transient state. The RIXS planes plot simple spin-wave calculations based on an increased thermal population of magnons after the pulse.

### Figure 2 | Destruction and recovery of charge and 3D magnetic order in Sr$_2$IrO$_4$. 

- **a.** Intensity of the $(-3,-2.28)$ magnetic Bragg peak 1 ps before (top panel) and 1 ps after (bottom panel) excitation at 6.8 mJ cm$^{-2}$. 
- **b, c.** Intensity of the magnetic Bragg peak as a function of probe delay focusing on the short (b) and long (c) timescales. The lines show the result of fitting the model, which incorporates one decay timescale and two recovery timescales. 
- **d.** Relative change in the 800 nm optical reflectivity ($\Delta R/R$) of Sr$_2$IrO$_4$ after excitation with a 620 meV pump at different fluences. All data are taken at 110 K. Error bars represent the statistical uncertainty in the intensities assuming Poisson counting statistics.

### Figure 3 | Time-resolved magnetic scattering. 

- **a.** Destruction and recovery of charge and 3D magnetic order in Sr$_2$IrO$_4$.
- **b.** Time-resolved X-ray magnetic scattering (RIXS) experiments using free-electron laser pulse and probe techniques such as X-ray magnetic dichroism$^{30}$, Faraday rotation$^{21}$ and the magneto-optical Kerr effect$^{22}$ capture only 3D magnetic order. This Letter breaks new ground by energy analysing the scattered X-rays, that is, by performing the first ever time-resolved (tr) magnetic resonant inelastic X-ray scattering (RIXS) experiment. RIXS probes the magnetic quasiparticle spectrum itself$^{23,24}$. This is a fundamental expression of the nature of the correlated electron state—as it is the spatial and temporal Fourier transform of the spin–spin correlation function and it encodes the interactions present in the magnetic Hamiltonian. In the present case of the 5$d$ valence electron compound Sr$_2$IrO$_4$, the relevant X-ray L-edge is in the hard X-ray regime, allowing full access to reciprocal space. Such Q-space resolution is not available in the complementary technique of time-resolved two-magnon Raman scattering, owing to the fact that visible photons carry negligible momentum$^{25}$. 

### Intensity in the Magnetic Bragg peak

This fluence corresponds to exciting a substantial fraction of all the lattice sites within the illuminated volume. Indeed, comparable fluences were also required to destroy long-range magnetic order in other strongly correlated materials, including manganites$^{26,28}$ and nickelates$^{27,28}$. 

To characterize the charge response to the 620 meV (2 µm) pump excitation, we measured the optical reflectivity at 1.55 eV (800 nm) in Fig. 2d. The photo-carrier recombination is dominated by processes in the picosecond or sub-picosecond regime, far faster than the recovery of 3D magnetic order, suggesting that the charge and magnetic recovery processes are largely independent of one another. 

A detailed understanding of ultrafast magnetic dynamics, beyond the presence or absence of 3D magnetic order, is severely hampered by limited experimental information regarding the short-range transient magnetic correlations. Other existing techniques such as X-ray magnetic dichroism$^{30}$, Faraday rotation$^{21}$ and the magneto-optical Kerr effect$^{22}$ capture only 3D magnetic order. This Letter breaks new ground by energy analysing the scattered X-rays, that is, by performing the first ever time-resolved (tr) magnetic resonant inelastic X-ray scattering (RIXS) experiment. RIXS probes the magnetic quasiparticle spectrum itself$^{23,24}$. This is a fundamental expression of the nature of the correlated electron state—as it is the spatial and temporal Fourier transform of the spin–spin correlation function and it encodes the interactions present in the magnetic Hamiltonian. In the present case of the 5$d$ valence electron compound Sr$_2$IrO$_4$, the relevant X-ray L-edge is in the hard X-ray regime, allowing full access to reciprocal space. Such Q-space resolution is not available in the complementary technique of time-resolved two-magnon Raman scattering, owing to the fact that visible photons carry negligible momentum$^{25}$.

### References

Figure 3 plots the RIXS energy loss spectra measured in Sr$_2$IrO$_4$ after photo-excitation at 6 mJ cm$^{-2}$, as compared to the unperturbed state 50 ps before excitation. The chosen pump fluence corresponds to what was required to destroy 3D magnetic order, as seen in Fig. 2a,b. The RIXS spectra show two dominant features, identified as magnon and orbital excitations\textsuperscript{9,26,27}, which we address in turn.

Orbital excitations appear in the RIXS spectra around 600 meV, and correspond to exciting a hole from the $2p$ state to $3d$ orbitals. Owing to the presence of residual photo-excited carriers in the transient state, we suggest that these carriers are directly responsible for damping the magnetic correlations around $\sim 100$ meV and causing an apparent redistribution of the magnetic spectral weight to lower energy.

Having clarified the 2D correlations in the transient state, we reassess the behaviour of the 3D magnetic order presented in Fig. 2. Even in the few picosecond regime (Fig. 2b), a small amount of magnetic recovery is evident. However, full recovery takes somewhere between 100 and over 1,000 ps (Fig. 2c). We found that a minimal model for the magnetic intensity as a function of time, $I(t)$, required one decay timescale $\tau_{\text{decay}}$ and two recovery timescales—which, for reasons that we will explain later, are labelled $\tau_{\text{I}}$ and $\tau_{\text{II}}$, where $\tau_{\text{I}} < \tau_{\text{II}}$

$$I(t) = I_0 \left( \exp(-t/\tau_{\text{decay}}) + C \left[ 1 - \exp(-t/\tau_{\text{I}}) \right] \right) + \left( 1 - C \right) \left[ 1 - \exp(-t/\tau_{\text{II}}) \right]$$

This model was fitted to the magnetic Bragg peak intensity data in Fig. 2b,c. In a similar way, we fitted the recovery of the optical reflectivity, which also required two charge timescales, denoted $\tau_{\text{I}}$ and $\tau_{\text{II}}$.

Figure 4 summarizes the magnetic and charge dynamics in Sr$_2$IrO$_4$ after laser excitation. 3D magnetic order decays in $0.30 \pm 0.03$ ps approximately independent of fluence (Fig. 4a),...
which roughly equals the jitter-limited time resolution of the experiment. This sets an upper limit on the timescale for the destruction of magnetic order in this system. The fast component of the charge recovery (Fig. 4b) is of a similar magnitude (0.27 ± 0.04 ps). In Fig. 4c, we plot the faster magnetic recovery timescale, which is ~1.7 ps and increases slowly with fluence. As discussed above, the 2D in-plane magnetic correlations recover on a picosecond timescale, so the lack of 3D magnetic order can be primarily attributed to the lack of coherence between the IrO planes. Or, equivalently, after a few picoseconds there is a large population of low-energy long-wavelength magnons that, on average, preserve the 2D Néel correlations. Consequently, we observe a large population of low-energy long-wavelength magnons that, with fluence (Fig. 4d), increasing up to 1.130 ps at 13.8 mJ cm−2.

The 2D magnetic correlations we observe are non-thermal in nature and recover on a picosecond timescale denoted \( \tau_{2D} \). A striking similarity between \( \tau_{2D} \) and the slower charge recovery timescale \( \tau_{slow} \) is seen in Fig. 4c. This may reflect the similar energy scale of the in-plane electronic hopping parameter, \( t_i \), and the magnetic exchange, \( J_\parallel \), which are fundamentally linked in strongly correlated materials such as these through \( J_\parallel \approx t_i^2 / U \), where \( U \) is the Coulomb repulsion. The behaviour of the long-range magnetic order, in contrast, depends on secondary processes, such as inter-plane magnetic coupling and the dissipation of the energy from the spins into other degrees of freedom.

This work shows that direct measurements of the 2D magnetic correlations are consequently crucial for a full understanding of magnetic dynamics in strongly correlated materials. While the continued improvement of free-electron lasers, tr-RIXS is set to play a crucial role in understanding how magnetic correlations dictate the properties of doped Mott insulators and how they can be effectively manipulated by light.

**Methods**

Methods and any associated references are available in the online version of the paper.

**References**


**Acknowledgements**

The X-ray scattering work by M.P.M.D., Y.C., V.T. and X.M.C. was supported by the US Department of Energy Basic Energy Sciences Division of Materials Science and Engineering. X.L. acknowledges financial support from MOST (No. 2015CB921302) and CAS (Grant No. XDB07020200) of China. P.J. acknowledges support by Laboratory Directed Research and Development (LDRD) Program 12-007 (Complex Modeling). I.K., D.C. and A.H.S. were supported by the US Department of Energy under Contract No. DE-AC02-06CH11357. S.W. acknowledges financial support from Spanish MINECO (Severo Ochoa grant SEV-2013-0352), Ramon y Cajal programme RYC-2013-14838, Marie Curie Career Integration Grant PCIG12-GA-2013-618487 and Fundació Privada Cellex. J.L. is sponsored by the Science Alliance Joint Directed Research and Development Program at the University of Tennessee. Work in London was supported by the EPSRC. The magnetic Bragg peak measurements were performed at the BL3 of SACLAC with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2014B8018). This research used the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, which is a DOE Office of Science User Facility, under Contract No. DE-AC02-76SF00515.

**Author contributions**


**Additional information**

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.P.M.D., Y.C. or X.L.

**Competing financial interests**

The authors declare no competing financial interests.
Methods

Samples. The magnetic Bragg peak measurements were performed on 200 nm epitaxial films of Sr$_2$IrO$_4$, to match the volume of Sr$_2$IrO$_4$ to the penetration depth of the pump, as the X-ray penetration depth is longer than the pump. The disappearance of the magnetic Bragg peak in Fig. 2a,b confirms that the whole probed volume is excited. The film was deposited on SrTiO$_3$ using pulsed laser deposition, as described in the Supplementary Information and ref. 33. Supplementary Figs 1 and 2 demonstrate good sample crystallinity and the lack of any detectable impurity phases. For RIXS, ~1° grazing incidence X-rays were used to limit X-ray penetration depths to 80 nm on a bulk Sr$_2$IrO$_4$ crystal. Both samples have a $c$-axis surface normal. Reciprocal lattice notations are defined using the full unit cell with lattice constants $a = b = 5.51$ Å and $c = 25.7$ Å. The high-symmetry points in the in-plane Brillouin zone are defined in the reduced structural zone (which ignores the rotation of the IrO$_6$ octahedra) as in ref. 9. The zone centre, denoted $(\pi, \pi)$ and the zone boundary denoted $(\pi, 0)$ correspond to $(1, 0, L)$ and $(0.5, 0.5, L)$, respectively, in the reciprocal lattice notation. In both experiments, the sample was cooled to about 110 K with a nitrogen cryostream, well below the Néel temperature of 240 K (ref. 13).

Optical pump. For both tr-REXS and tr-RIXS experiments, 100 fs pump pulses were generated at 620 meV (2 μm) using an optical parametric amplifier. The pulses were polarized vertically in the ab-plane of the sample and were incident at 13° with respect to the sample surface. The choice of pump energy follows previous optical conductivity measurements and resonates between the upper and lower Hubbard bands.

The time-resolved resonant elastic X-ray scattering (tr-REXS) set-up. The tr-REXS experiment was performed at beamline 2 of the SFring-8 Angstrom Compact free-electron Laser (SACLAC) with a 30 Hz pulse repetition rate. We adopted a horizontal scattering geometry, as seen in Fig. 1a, and tuned the X-ray energy to the peak in the Ir L$_3$ edge resonance around 11.215 keV. A multi-port charged coupled device (MPCCD) area detector was placed at 2θ = 88.7° to observe the magnetic Bragg peak ($-3, -2, 28$). This geometry is chosen to optimize the X-ray resonant magnetic scattering cross-section. We access the magnetic peak by rotating the sample around the vertical axis by $\phi = 12.8°$, with the infrared and X-ray photons in an approximately co-linear geometry. The detector was read out shot by shot and the signal was thresholded to suppress the background coming from X-ray fluorescence and electrical noise. The peak intensity was determined by binning the 2D MPCCD data into a 1D spectrum and fitting a Lorentzian lineshape with a uniform offset background. Each datapoint is the result of summing 1,000–4,000 shots. Previous characterization of the beamline found that the time resolution of this experiment was jitter-limited to approximately 300 fs.

The minimal model for the fitting is outlined in the main text (equation (1)). This formula was convolved with a 100 fs Gaussian to account for the pump pulse width. The other major contribution to the effective time resolution was the X-ray pulse jitter of approximately 300 fs, because this is only an approximate value this was not included in the fit, rather this is taken as an upper limit on the decay time. Apart from this quantity, all parameters were varied to fit the data in the long time–delay scans at 1.6, 2.7 and 13.8 μJ cm$^{-2}$ fluence in Fig. 2c, and these fits were used to constrain $\tau_{\text{dec}}$ in fits of the short-time–delay data in Fig. 2b by interpolating the variation of $\tau_{\text{dec}}$ and C as a function of fluence. In this way, equation (1) provides an accurate parametrization of the recovery dynamics at all fluences studied.

The time-resolved resonant inelastic X-ray scattering (tr-RIXS) set-up. The tr-RIXS experiment was performed at the X-ray pump probe instrument at the Linac Coherent Light Source (LCLS) with a 120 Hz repetition rate. We adopt a horizontal scattering plane, similar to the set up in the tr-REXS experiment. The $(\pi, 0)$ and $(\pi, \pi)$ data were measured at (~$-3.5, -3.5, 24.1$) and (~$-4, -3.23.9$). Non-integer values of $L$ were chosen to keep the X-ray incidence angle around 1°, as the RIXS spectrum is known to be essentially independent of $L^2$. A Si (333) monochromator produced a 50 meV incident energy bandwidth. The RIXS spectrometer is conceptually similar to that used at Sector 27 at the Advanced Photon Source. Scattered photons from the sample are reflected from a segmented spherical Si(8, 4, 4) analyser in a near-backscattering configuration and detected by a Princeton CCD. The sample, the analyser crystal, and the photodetector are placed on a Rowland circle with a radius of 1 m in the vertical plane. The total energy resolution of the tr-RIXS set-up was ~70 meV and the Q resolution was defined by the ~6° angular acceptance of the analyser. RIXS spectra were collected in a stationary mode without moving the spectrometer, and the pixel-to-energy conversion was performed using well-established methods. The CCD was read out every 1,800 shots. Jitter and timing drift were the main contributions to the time resolution, which was on the order of 500 fs.

References