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Letter

Ultrafast dynamics of localized magnetic moments in the unconventional Mott insulator Sr_2IrO_4

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Abstract

We report a time-resolved study of the ultrafast dynamics of the magnetic moments formed by the $J_{\mathrm{eff}} = 1/2$ states in Sr_2IrO_4 by directly probing the localized iridium 5*d* magnetic state through resonant x-ray diffraction. Using optical pump–hard x-ray probe measurements, two relaxation time scales were determined: a fast fluence-independent relaxation is found to take place on a time scale of 1.5 ps, followed by a slower relaxation on a time scale of 500 ps–1.5 ns.

Keywords: iridates, spin–orbit coupling materials, free-electron laser science, resonant diffraction, ultra-fast x-ray studies, magnetism

(Some figures may appear in colour only in the online journal)

1. Introduction

Mott physics based on strong on-site Coulomb repulsion U, coupled with small electronic bandwidth W, is at the heart of fascinating physical phenomena such as high-temperature superconductivity, metal-insulator transitions and colossal magnetoresistance [1]. The spatial delocalization of 4*d* and 5*d* states is believed to reduce correlation effects, however anomalous insulating behavior has been reported in numerous 4*d* and 5*d* transition metal oxides, such as Ca_2RuO_4 and $Cd_2Os_2O_7$ [2, 3]. A natural candidate to explain this is the significant spin–orbit coupling (SOC) strength [4], about 0.4 eV in heavy transition-element systems [5].

The iridium oxides are an especially interesting class of 5*d* electron systems because new exotic phases are predicted to exist [6, 7], such as the 'topological Mott insulator' state [8], with novel physics as described in the quantum compass model [5] or the Kitaev model on a honeycomb lattice [9].

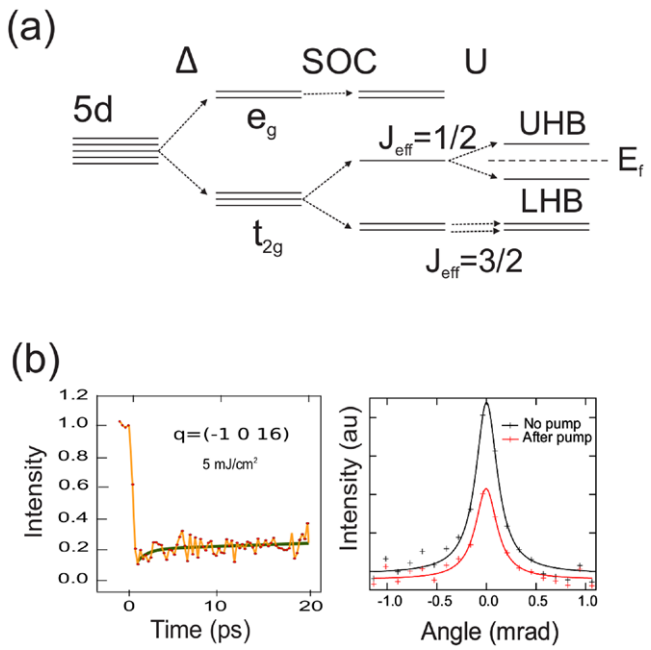

Figure 1. (a) Schematic diagram of the 5*d* energy levels split by the crystal field (Δ), spin–orbit coupling (SOC), and on-site Coulomb repulsion (U) leading to the formation of the unoccupied (upper) and occupied (lower) Hubbard bands around the Fermi level from the $J_{\rm eff} = 1/2$ band and the fully occupied $J_{\rm eff} = 3/2$ band. (b) Data showing the time dependence of the $q = (-1\ 0\ 16)$ magnetic peak reflecting the ordering of the $J_{\rm eff} = 1/2$ states after optical excitation at 5 mJ cm^{-2} out to 20 ps (left). The width of the magnetic diffraction peak at the L_3 absorption edge, before and after the optical excitation (right).

The close proximity of energy scales [10] that exists among the spin–orbit interaction energy together with the Coulomb interactions and electron bandwidth also make the iridates a particularly unique class of materials to study relating to emergent phenomena. Structurally, the iridates tetragonal crystal symmetry (space group $I4_1/acd$)[10], maps onto the parent compounds La_2CuO_4 and Sr_2RuO_4 of the doped high-temperature cuprate and *p*-wave superconductors, respectively [12]. This correlation has drawn much attention to the magnetic degree of freedom in these materials since it has been proposed as one of the potential pairing mechanisms in the high temperature superconductors. Theoretical predictions on the existence of a superconducting state in the phase diagram of doped Sr_2IrO_4 have also been made [13–15] and were followed by STM work [16] and the finding of a d-wave gap in electron-doped Sr_2IrO_4 [17], but the observation of superconductivity to date has remained elusive.

At the forefront of recent investigations is Sr_2IrO_4, where a novel ground state $J_{\rm eff} = 1/2$ has been identified [18]. The strong spin–orbit coupling inherited from the Ir ions entangles the t_{2g} spin and orbital states leading to the formation of $J_{\rm eff} = 1/2$ and $J_{\rm eff} = 3/2$ states. Moreover, electron correlations split the $J_{\rm eff} = 1/2$ levels into separate upper Hubbard (UHB) and lower Hubbard bands (LHB) near the Fermi level (see figure 1(a)) [19]. As a result of spin–orbital mixing on the 5*d* orbitals, the interactions between the $J_{\rm eff} = 1/2$ states strongly depend on the lattice geometry, which can induce broad classes of states. The magnetic interactions are highly anisotropic [20, 21] and are governed by a nearly Heisenberg-like Hamiltonian [22]. In contrast to the conventional situation in the 3*d* materials, where the spin–orbit interaction is only a perturbation on the magnetic interactions and whose isotropic nature is of SU(2) symmetry, the anisotropy of Sr_2IrO_4 appears only via Hund's rule coupling. The magnetic degree of freedom can be described by a single ion Hamiltonian with the lowest energy levels being the Kramers doublet of isospin states formed by the coherent superposition of spin and orbitals states [5]. Interestingly, this magnetic Hamiltonian allows for additional magnetic excitations in the low energy spectrum, namely the spin–orbital wave (often referred to as the 'spin–orbiton') in addition to conventional magnon wave excitations [22–24].

In this letter, we directly trace out the behavior of the 5*d* electron states of the iridium atoms via time-resolved measurements tuned to the magnetic spin states of an iridate Mott insulator. We perform first ultrafast pump–probe experiments with x-ray radiation using resonant x-ray diffraction (XRD), probing the antiferromagnetically ordered ground state in Sr_2IrO_4 on an ultrashort time scale. Resonant XRD is directly sensitive to local 2*p*-to-5*d* transitions, providing information on the behavior and dynamics of the $J_{\rm eff} = 1/2$ manifold. We experimentally deduce a strong mixture of local and itinerant states by observing relaxation dynamics 'locked' to the same timescale of ∼1.5 ps, irrespective of the level of pulse energies used in our experiment, which are shown to greatly alter the long timescales of the magnetic structure.

2. Experimental

Epitaxial thin films of Sr_2IrO_4 were grown on a $SrTiO_3$ substrate using the flux method [19]. Because the optical laser penetration depth (about 100 nm) and the hard x-ray penetration depth (about 60–70 microns) are so different, the film thickness was chosen to be 100 nm to ensure the full volume of the film being studied could be optically excited. In all our measurements, an ultrafast optical pump pulse ($1/e^2$ width of ∼590 μm) of 1.55 eV illuminates the sample to excite the electronic system out of equilibrium and then, after a controlled time delay (Δt), a probe pulse (∼295 μm) is used to probe the evolution of the excited non-equilibrium state. Measurements consisted of XRD using ultra-short pulses from the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory [25] and were performed at the sample temperature of 150 K. The intensity of the magnetic diffraction peak was recorded as a function of the time delay between the infrared optical laser pulse (50 fs pulse duration) and the hard x-ray probe FEL pulse (see figure 1(b)). The x-ray energy was tuned to the resonance energy of the iridium L_3 edge ($h\nu = 11.215$ keV). The third harmonic of the XPP instrument monochromator at LCLS [26] was used to reach this energy. The pulse repetition rate of the FEL was 120 Hz. The low temperature $(-1\ 0\ 16)$ magnetic

[10] Note: recent neutron scattering work seems to suggest the crystal structure might be space group $I4_1/a$ in rhodium-doped iridates, see Ye *et al* [11].

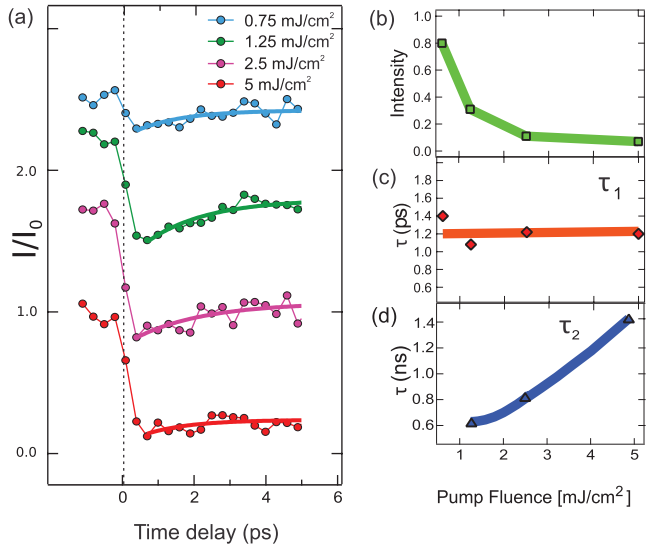

Figure 2. (a) Magnetic relaxation dynamics measured by the response of the magnetic peak at the iridium L-edge. The curves are shown as a function of excitation fluence over the first 5 ps. The time traces are normalized to before the excitation pulse with all curves offset from the highest fluence for clarity. (b) Normalized peak intensity immediately after optical excitation, (c) associated fast time constants for different pump fluences, as resulted from the double exponential fit together with (d) the slow time constants. By comparing the two time constants, it is evident that the slower times are strongly fluence dependent.

diffraction peak was chosen among previously observed (1 0 $4n + 2$), (0 1 $4n$) and (0 0 $2n + 1$) magnetic peaks [19], due to its higher intensity at the L_3 edge.

3. Results

The effect of the optical excitation on the magnetic diffraction peak is demonstrated in figure 1(b). The peak intensity drops sharply upon the optical excitation followed immediately by recovery dynamics. It is noteworthy that the position and the width of the magnetic peak do not show any measurable variations over the parameters chosen for this experiment upon optical excitation. This indicates that the periodicity and the correlation length of the antiferromagnetic structure shows no variation in the optically excited state. This behavior is in sharp contrast to thermal excitation which conventionally leads to broadening of the diffraction peak due to shortening of the correlation length. It also strongly suggests that on the time scales of interest in our experiment, thermal effects are minimal. Therefore even though the electronic bath is heated significantly during the photoexcitation process, the transient effects are non-thermal, implying the electronic system is still below the Neel temperature on this timescale.

Figure 2(a) shows the time-resolved transient change of integrated intensity of the (−1 0 16) magnetic diffraction peak associated with the antiferromagnetic ordering of the $J_{\text{eff}} = 1/2$ states in the insulating phase of Sr_2IrO_4. Time traces are recorded after the excitation with an IR optical laser pulse in the pump fluence regime of 0.75–5 mJ cm^{-2}. Impulsive reduction of the peak intensity at zero time delay reflects excitation of the antiferromagnetic structure of the system to a non-ordered, non-equilibrium state (see figure 2(b)). The observed leading edge width of the intensity variation is about 300 fs and is limited by jitter between the x-ray and optical laser pulse arrival times, considered here as an upper limit for the excitation time scale. The system immediately starts to recover in the form of a double exponential observed in the data. The curves characterizing the recovery dynamics of the magnetic peak give a fast relaxation time scale of about 1.5 ps, showing no dependence on the pump fluence (see figure 2(c)). The slow component of the relaxation dynamics gives a nearly-linear time constant in the range of 500 ps–1.5 ns (see figure 2(d)).

The prompt suppression of magnetism indicates that optical photoexcitation directly leads to disordering of the antiferromagnetic state, quite likely by creating electron–hole (e–h) pairs across the Mott gap. The fluence-independent recovery of magnetism during the fast relaxation process indicates that the initial decay is not caused by electron thermalization. Rather it is more likely due to cooling mediated by non-thermally occupied phonons [27]. Therefore we ascribe the fast magnetic dynamics to rapid cooling of electrons by emission of hot phonons, which further decay to other low energy modes. After ∼5 ps, the system enters a regime of fluence-dependent relaxation, which indicates that further recovery of the magnetic order is dominated by the energy deposited by the pump pulse. Physically, this is due to the decay of the hot optical phonons into other low-energy modes, e.g low-energy phonons via anharmonic coupling. This coupling represents the limiting mechanism for the full recovery of the antiferromagnetic order.

4. Discussion

Immediately after the optical excitation the system is in a highly excited, non-thermal state and, due to very strong electron-phonon coupling, a large density of hot optical phonons is rapidly generated. On a longer timescale, the recombination rate is found to be proportional to the density of photoexcited electron–hole pairs (see figure 2(d)). Such behavior is typically indicative of a fully-formed energy gap [28], where photoexcited electrons can only combine with empty states below the Fermi energy and, with the larger density of e–h pairs, an increased recombination speed takes place.

On very short ⩽1 ps timescales, it is not clear if the system indeed becomes metallic. If a metallic state was induced, a much more rapid decay of the hot electrons is anticipated [27], since in a gapless state the system can very efficiently relax through interaction of both optical and acoustic phonons. The absence of this fast relaxation leads us to believe that the system remains in a gapped, insulating state even when strongly perturbed. This interpretation is supported by the XRD data where the signal is seen to begin recovering immediately after photoexcitation, indicating that the system spends very little time, if any, in the metallic phase. This is a much different response than what has been seen in the traditional metal-to-insulator system of magnetite for instance, where an optical pump fluence of 1.3 mJ cm^{-2} was able to

switch the insulating system to a metal for a relatively long period of time [29]. Thus we conclude that Sr_2IrO_4 displays a rather robust electronic structure regardless of significant impulsive photo-doping, possibly due to the strong electron-correlation effects responsible for the formation of the Mott-insulating gap or the interplay of the Hunds rule coupling with spin–orbit coupling [30].

5. Conclusion

We have performed direct studies of the dynamics of the $J_{\rm eff} = 1/2$ magnetic states residing on the 5*d* electrons in the insulating phase of Sr_2IrO_4. Two characteristic regimes for magnetic relaxation were determined: a fast, fluence-independent relaxation of ∼1.5 ps, followed by a slow, fluence-dependent relaxation on a timescale of 500 ps–1.5 ns. The initial, ultrafast suppression of the magnetic peak is likely due to photo-excitation of doubly occupied sites which reduces the long-range magnetic ordering. The ensuing dynamics in the first few picoseconds of both delocalized e–h pairs and localized magnetic moments proceed on a similar timescale, indicative of a very strong mixing of atomic and band-like contributions to the ground state in this system.

Potentially interesting physics can be further studied at shorter timescales. Future work is needed in this area to measure ultrafast dynamics at much better than 1 ps. Furthermore, the antiferromagnetic order can be perturbed by generation of magnons and spin–orbit excitons, and more advanced techniques are needed to be sensitive to these excitations, such as time-resolved resonant inelastic x-ray scattering. The direct measurements of magnetization dynamics outlined here further present a test for novel models [31] by providing information on relevant timescales and on the strength of magnetic interactions in iridates, a fast-growing area of scientific importance [32].

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