Ultrafast Hopping Dynamics of $5f$ Electrons in the Mott Insulator UO_2 Studied by Femtosecond Pump-Probe Spectroscopy

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We describe a femtosecond pump-probe study of ultrafast hopping dynamics of $5f$ electrons in the Mott insulator UO_2 following Mott-gap excitation at temperatures of 5–300 K. Hopping-induced response of the lattice and electrons is probed by transient reflectivity at mid- and above-gap photon energies, respectively. These measurements show an instantaneous hop, subsequent picosecond lattice deformation, followed by acoustic phonon emission and microsecond relaxation. Temperature-dependent studies indicate that the slow relaxation results from Hubbard excitons formed by $U^{3+} - U^{5+}$ pairs.

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Because of its important role as nuclear fuel, uranium dioxide (UO_2) has been extensively studied for several decades, with intensive experimental [1] and computational [2–5] efforts on its material properties. It is known that the $5f$ electrons in UO_2 play a critical role in understanding its thermodynamic, electronic, and magnetic properties, but their Coulomb correlations have been elusive. Before recognition of the strong correlation between $5f$ electrons, investigations indicated that UO_2 was a magnetic semiconductor [1], as opposed to a Mott insulator, as revealed by improved spectroscopic techniques [6–8] and theoretical modeling [2,9]. Femtosecond (fs) pump-probe spectroscopy permits the study of ultrafast dynamics of correlated electrons. Understanding such dynamics in cubic structured UO_2 should clarify the nature of $5f$ electrons and provide insight into the origin of superconductivity in heavy fermion U compounds [10] and quantum correlation physics in ultracold atoms [11].

In UO_2 the strong correlation characterized by the large on-site Coulomb repulsion of ~3 eV [12,13] splits a $5f$ band into a lower and an upper Hubbard band (LHB and UHB) [14] and forms a Mott gap (optical gap of ~2 eV [1,15]). In the ground state, the LHB is occupied and the UHB empty, and two electrons are localized on each U site to form a highly ionic $U^{4+}(5f^2)$. Low-energy excitations across the Mott gap are therefore of intersite $5f$-$5f$ hopping character. The excitation creates a U^{3+} and U^{5+} pair:

$$2U^{4+}(5f^2) \rightarrow U^{3+}(5f^3) + U^{5+}(5f^1), \quad (1)$$

which may form either a bound state, such as a Hubbard exciton [16,17], or remain decoupled, depending on the competition between Coulomb energy and kinetic energy. If lattice deformation is induced around U^{3+} and U^{5+}, polarons or polaronic excitons may form [12,18].

Here we present a fs pump-probe study of hopping dynamics of $5f$ electrons in UO_2, in which a pump pulse at 3 eV initiates intersite hopping of $5f$ electrons, and a time-delayed pulse, at either 1.5 or 3 eV, probes the evolution of the lattice or excited electrons, respectively. We perform transient reflectivity measurements over a temperature (T) range of 5–300 K with emphasis on the antiferromagnetic (AFM) transition at the Néel temperature of $T_N = 30.8$ K [1]. We observe an instantaneous response for intersite hopping of $5f$ electrons, followed by a picosecond (ps) response for lattice deformation, acoustic phonon emission, and its long-lived propagation in the sample. We find a slow relaxation process on microsecond (μs) time scales and assign it to the decay of Hubbard excitons formed by neighboring $U^{3+} - U^{5+}$ pairs.

The experiment was carried out with a 250-kHz Ti: sapphire regenerative amplifier producing 6 μJ, 80 fs pulses at 1.5 eV. The 3-eV pulses were generated by frequency doubling the fundamental for pumping or probing above the Mott gap. The pump fluence (F) ranged from 0.5–70 $\mu J/cm^2$ and the probe, ~13 $\mu J/cm^2$. Transient reflectivity was measured by varying the time delay between the pump and probe pulses when spatially overlapped on the sample. The fractional change of the probe reflectivity, $\Delta R/R$, was detected by a photodiode and then fed into a lock-in amplifier for high sensitivity measurements. The pump and probe pulses were S/P cross polarized to suppress noise from scattering. The sample was a 1-mm-thick, (100) surface-oriented single crystal of UO_2 mounted in a liquid He cooled cryostat for measurements at low temperatures.

Figure 1 shows the measured 1.5-eV reflectivity transients, $\Delta R/R$, of UO_2 at several different temperatures for a fixed pump fluence $F = 64$ $\mu J/cm^2$ as a function of the time delay t between the pump and probe pulses. Each transient contains three stages: the initial 60 ps revealing the detailed rise process plus the first oscillation cycle, up to 0.9 ns showing damped oscillations, and 27–28 ns showing persistent relaxation after a long delay. Negative transients indicate photoinduced absorption. The initial ps rise appears to be an exponential with an amplitude, A_0, initially offset from zero by A_{off}, and a time constant, τ_{rise}, as

$$\Delta R/R = A_0 - (A_0 - A_{\text{off}})e^{-t/\tau_{\text{rise}}}. \quad (2)$$

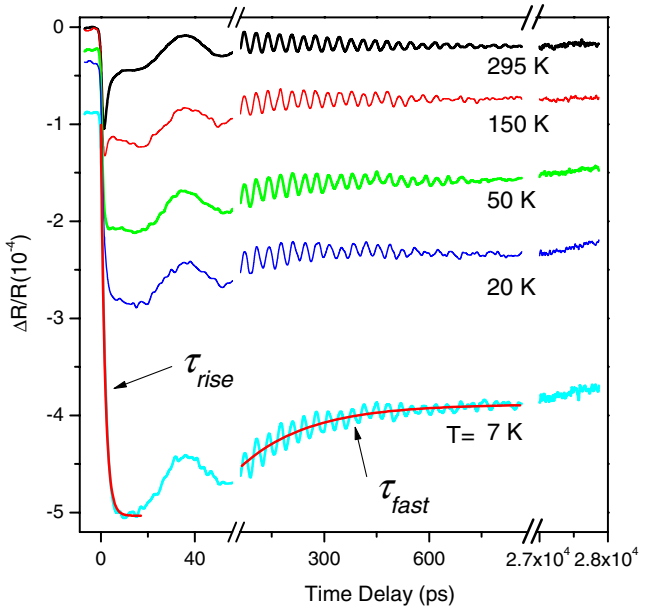

FIG. 1 (color online). Measured 1.5-eV reflectivity transients of UO_2 at different temperatures. Smooth lines are exponential fits for the rise time, $\tau_{\rm rise}$, and the fast relaxation time, $\tau_{\rm fast}$, at a temperature $T = 7$ K.

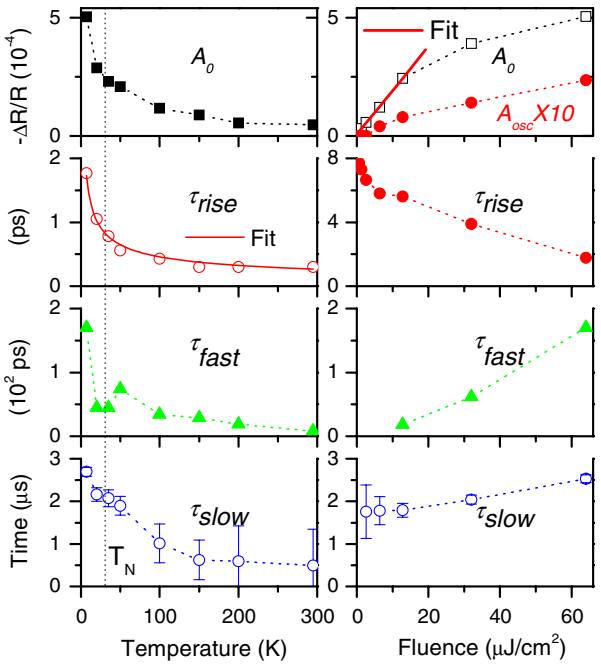

FIG. 2 (color online). Left panel: Temperature dependence of the rise amplitude, A_0, and time constants, $\tau_{\rm rise}$, $\tau_{\rm fast}$, and $\tau_{\rm slow}$, at a pump fluence $F = 64$ μJ/cm^2, extracted from 1.5-eV reflectivity transients. Right panel: Fluence dependence of the above parameters and the oscillation amplitude, $A_{\rm osc}$, at a temperature $T = 7$ K. A linear fit of $A_0(F)$ and a $1/T^{1/2}$ curve fit of $\tau_{\rm rise}(T)$ are included. Error bars are added for $\tau_{\rm slow}$.

The relaxation can be represented by the sum of three terms: both fast and slow decaying exponentials, and a damped oscillation, with respective time constants, $\tau_{\rm fast}$, $\tau_{\rm slow}$, and $\tau_{\rm osc}$, as

$$\Delta R/R = A_1 e^{-t/\tau_{\rm fast}} + A_2 e^{-t/\tau_{\rm slow}} + A_{\rm osc} e^{-t/\tau_{\rm osc}} \cos(2\pi f t - \delta). \quad (3)$$

Here A_n are the component amplitudes, f the oscillation frequency, and δ the phase.

The oscillation term in Eq. (3) exhibits a frequency of 29.4 GHz consistent with $f = 2n\upsilon/\lambda$ where $n = 2.31$ and $\upsilon = 5294$ m/s at 300 K [1,19], corresponding to an acoustic phonon packet propagating into the sample [4,20]. Here n and κ are, respectively, the real and imaginary parts of the refractive index at the probe wavelength λ and υ, the speed of sound. The observed $A_{\rm osc}$ and f vary negligibly with T. The near normal incidence reflectivity, $R(T)$, was measured and found to be decreasing linearly from 16% to 13.5% between 300 and 5 K, resulting in a decrease in $n(T)$ and an increase in $\upsilon(T)$ of ~7.4%, which means that the lattice becomes less flexible at lower T. The continuity of $\upsilon(T)$ likely indicates the absence of structural phase transitions in unexcited UO_2, such as Jahn-Teller distortions [21]. The observed large $\tau_{\rm osc} = \lambda/4\pi\upsilon\kappa$ of ~0.3 ns and small $\delta \approx \kappa/n$ of ~0 [20] confirm that the probe is well below the Mott gap for the entire T range.

The left panel of Fig. 2 shows the T dependence of the rise amplitude, A_0, and the rise and relaxation time constants, $\tau_{\rm rise}$, $\tau_{\rm fast}$, and $\tau_{\rm slow}$, which are extracted from the fits of the measured 1.5-eV reflectivity transients at a fixed pump fluence $F = 64$ μJ/cm^2 using Eqs. (2) and (3). The right panel of Fig. 2 shows the F dependence of the above parameters and the oscillation amplitude, $A_{\rm osc}$, at a fixed $T = 7$ K. All T-dependent parameters increase upon cooling except for an anomaly of $\tau_{\rm fast}$ around T_N. For the F-dependent parameters, $\tau_{\rm rise}$ decreases but all others increase with increasing F.

The behavior of the rise amplitude, A_0, is understood in terms of photoinduced midgap states. The absorbed pump energy into UO_2 thermalizes the $5f$ electron subsystem to an elevated electronic temperature T_e within 80 fs, while the lattice stays at the ambient temperature T. During $\tau_{\rm rise}$, excited electrons dissipate energy into the lattice and cause lattice deformation around U^{3+} and U^{5+}, which then generates transient midgap states. The maximum density of the midgap states is reached at the largest deformation, resulting in the rise amplitude, A_0, presumably proportional to $T_e - T$. The observed large amplitude increase of $A_0(T)$ on cooling is due to a slower decrease of T_e. The measured $A_0(F)$ fits as a straight line at lower F but quickly deviates from linearity at higher F, indicating that 1.5-eV photons probe hopping-induced lattice effects.

The T and F dependences of the characteristic rise and relaxation times reflect lattice dynamics and electron correlation. A longer $\tau_{\rm rise}(T)$ at lower T means more time is needed for electron-lattice thermalization when the lattice

is rigid. $\tau_{\text{rise}}(T)$ can be fit as $1/T^{1/2}$, as shown in Fig. 2, which describes the T-dependent trend of the hopping duration of a polaron [12], indicative of the time for lattice distortion. The fast relaxation time $\tau_{\text{fast}}(T)$ results from the expanding of lattice distortion into the unexcited UO_2 during 100 ps timeframes, as the distortion amplitude following excitation decreases exponentially along the sample depth. The anomalous drop of $\tau_{\text{fast}}(T)$ around T_N indicates the restoration of AFM correlation (the spin-lattice relaxation) following the lattice disturbance. When thermal excitation is nearly quenched at $T = 7$ K, a shorter $\tau_{\text{rise}}(F)$ at higher F means less time with more energy for lattice deformation, and a longer $\tau_{\text{fast}}(F)$ or $\tau_{\text{slow}}(F)$ at higher F means more excitonic states and more interaction among them. Persistent oscillations at low F indicate strong coupling between hopping electrons and the lattice.

A nonzero offset, represented by A_{off} in Eq. (2), of $\Delta R/R$ at zero time delay $t = 0$, is apparent in Fig. 1 at low T, meaning that the prior pump pulse (4 μs ahead) contributes to a residual ΔR. If we assume an exponential decay for $\Delta R/R$, we can calculate τ_{slow} using the transient data at $t = 0.8$ ns and $t = 4$ μs. At high T, A_{off} falls to zero or into noise levels because of limited sensitivity. Additionally, we add an extra time delay of 27 ns and then calculate τ_{slow} using the transient data at $t = 0.8$ ns and $t = 27$ ns. Remarkably, we find that τ_{slow} is on μs time scales, as shown in Fig. 2, much longer than ps to ns relaxation times observed on $3d$ transition metal oxides [22].

To directly probe the behavior of photoexcited $5f$ electrons in the UHB, we change the probe photon to 3 eV but use the same pump energy of 3 eV. Figure 3 shows the measured 3-eV reflectivity transients, $\Delta R/R$, of UO_2 at several different temperatures for a fixed pump fluence $F = 64$ μJ/cm^2. Oscillations in the transients are barely observable because of absorption of the probe within a 100 nm skin depth [1]. An average of six transients at $T = 295$ K is shown in the inset of Fig. 3. The half-frequency of the oscillations confirms the presence of acoustic phonons represented in Eq. (3). The small damping constant and large phase of the oscillations result from a large imaginary part (κ) of the refractive index.

The initial relaxation stage of the 3-eV reflectivity transients is fit to a decaying exponential with an amplitude, A_{flat}, and a time constant, τ_{relax}. The slow relaxation time appears shorter than those probed by 1.5-eV photons but still occurs on μs time scales. All transients show an abrupt, positive rise, indicating that the electron hop happens within 80 fs (the pulse duration or time resolution). The transients fall into a flat region of the amplitude, A_{flat}, during τ_{relax}. When $T < T_N$, τ_{relax} actually includes two stages: a relaxation towards zero and a rise towards a negative maximum, but we treat it as a single relaxation term for simplicity. The T dependence of A_{flat} and τ_{relax} at $F = 64$ μJ/cm^2 are plotted in the left panel of Fig. 4, and the F dependence of them at $T = 7$ K are in the right panel. $A_{\text{flat}}(F)$ fits linearly over a larger F range than for the 1.5-eV probe, because the number of excited $5f$ electrons is proportional to F. $\tau_{\text{relax}}(T)$ decreases on lowering T, but $\tau_{\text{relax}}(F)$ does not exhibit monotonic behavior. $A_{\text{flat}}(F)$ does not cross zero, but $A_{\text{flat}}(T) = 0$ at T_N,

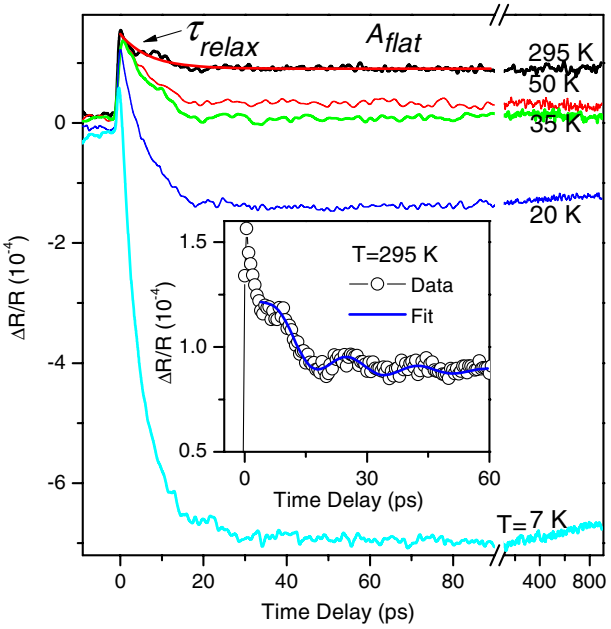

FIG. 3 (color online). Measured 3-eV reflectivity transients of UO_2 at different temperatures. Inset: An average of six transient scans and a fit of damped oscillations at 295 K. The smooth line on $T = 295$ K is an exponential fit for the initial relaxation time, τ_{relax}, and the flat amplitude, A_{flat}.

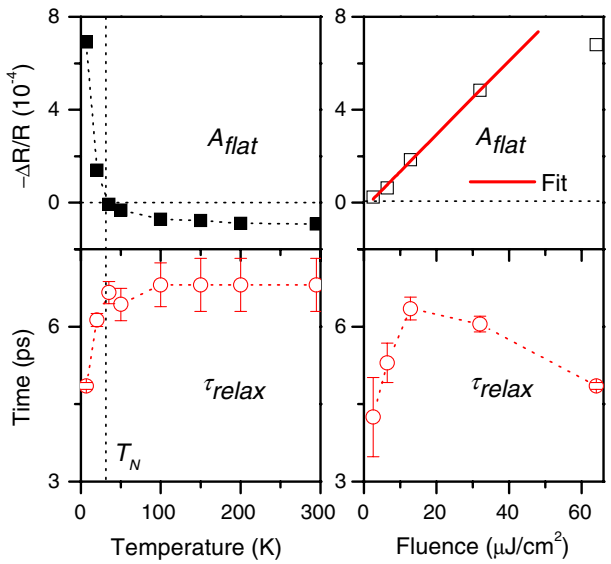

FIG. 4 (color online). Left panel: Temperature dependence of the flat amplitude, A_{flat}, and the initial relaxation time, τ_{relax}, at a pump fluence $F = 64$ μJ/cm^2, extracted from 3-eV reflectivity transients. Right panel: Fluence dependence of the parameters at a temperature $T = 7$ K. A linear fit of $A_{\text{flat}}(F)$ is included. Error bars are added for τ_{relax}.

suggesting that $A_{\text{flat}}(T)$ intrinsically characterizes the magnetic order.

The T and F dependences of τ_{slow} in Fig. 2 suggest the formation of Hubbard excitons during the relaxation. Analogous to one-dimensional extended Hubbard models [16], the Hubbard model in the fcc lattice of U^{4+} can be considered to contain neighbor Coulomb interactions, and thus allows Hubbard excitons [16,17] of bound pairs of nearest-neighbor U^{3+} and U^{5+}, written as $U^{3+} - U^{5+}$. Unbound U^{3+} and U^{5+} pairs may also be created following excitation. They should have a recombination time strongly dependent on the initial number of pairs (or F), but the observed $\tau_{\text{slow}}(F)$ at 7 K is very flat. The result indicates that the μs relaxation time arises from bound pairs only and that the pairing occurs during the initial relaxation time of τ_{relax}. In the noncollinear 3-k AFM structure of UO_2 [5,23], the magnetic moments of nearest neighbors U^{4+} form a relative angle of 109°, which hinders the hopping of an excited electron to its nearest neighbor because a spin-flip is involved and thus slows down the recombination of a bound pair $U^{3+} - U^{5+}$. When $T > T_N$, thermal motion assists the spin-flip and breaks the binding of U^{3+} and U^{5+}, resulting in a quick drop of the observed relaxation time $\tau_{\text{slow}}(T)$.

The observed zero crossing of $A_{\text{flat}}(T)$ at T_N and the decrease of $\tau_{\text{relax}}(T)$ at low T in Fig. 4 follow as a consequence of Hubbard excitons in UO_2. When $T > T_N$, excited $5f$ electrons in the UHB are free to hop to neighboring sites, similar to itinerant carriers in semiconductors as seen by optical conductivity, and thus, contribute a $\Delta R > 0$. When $T < T_N$, $5f$ electrons are depleted because they form excitons, resulting in a fast drop in conductivity and thus $\Delta R < 0$. The observation that $\tau_{\text{relax}}(T)$ appears flat when $T > T_N$ but decreases rapidly when $T < T_N$ is explained by the hypothesis that the magnetic pairing of U^{3+} and U^{5+} overwhelms the intra-UHB relaxation where $\tau_{\text{relax}}(T)$ is an interplay of the two processes. The apparent maximum of $\tau_{\text{relax}}(F)$ supports such a scenario of competing processes.

Our results show that the hopping of $5f$ electrons in UO_2 happens in less than 80 fs, but is followed by an intra-UHB relaxation, simultaneous lattice deformation, and if $T < T_N$, the binding of $U^{3+} - U^{5+}$, all on ps time scales. The intersite hopping induces strong electron-lattice interaction as indicated by coherent acoustic phonon emission over a wide range of temperatures and excitation levels. The relaxation is found to be unusually slow, on μs time scales, and is attributed to Hubbard excitons of $U^{3+} - U^{5+}$ pairs. The behavior of the transient reflectivity around T_N shows that the pairing of $U^{3+} - U^{5+}$ is mediated through magnetic ordering, a signature of Hubbard excitons.

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