Pump-probe reflectivity study of ultrafast dynamics of strongly correlated 5f electrons in UO₂

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Abstract. 5f electrons in the Mott insulator UO₂ produce intriguing electronic states and dynamics, such as strong correlation and f-f excitations. We have performed femtosecond pump-probe reflectivity measurements on a single crystal UO₂ at temperatures of 5-300 K to study the ultrafast dynamics of photoexcited 5f electrons. Laser pulses at 400 nm pump 5f electrons across the Mott gap, while those at 800 nm probe the pump-induced change of reflectivity. We find temperature-dependent excitation and relaxation processes and long-lived acoustic phonons, and extract picosecond risetimes and microsecond relaxation times at low temperatures. The observed slow relaxation is ascribed to the decay of Hubbard excitons formed by U³⁺-U⁵⁺ pairs.

1. Introduction

The simple cubic uranium dioxide (UO₂) is a model system for the understanding of electronic transport properties, thermodynamics, and magnetism of 5f materials, and such understanding is also fundamental for strongly correlated electron physics of Mott insulators in general. For decades UO₂ has been extensively studied both experimentally [1] and computationally [2, 3], mainly due to its important role as nuclear fuel. In the earlier review of its optical properties and electronic structures by J. Schoenes [1], UO₂ was regarded as a magnetic semiconductor with a bandgap about 2 eV, without recognition of the Mott-insulating nature of its ground state. Spectroscopic techniques and theoretical modeling have made progress in accessing the specific atomic arrangement and electronic structure [3-5], suggesting UO₂ as a Mott insulator. It has an antiferromagnetic (AFM) ground state and a magnetic transition at the Neel temperature, T_N=30.8 K. Photoexcitation in a Mott insulator may involve carrier hopping between localized states, while that in a band insulator locally creates itinerant carriers.

Because of the strong electron correlation characterized by large on-site Coulomb repulsion U (~3 eV) [6], a Mott gap is formed between an occupied lower Hubbard band (LHB) and an unoccupied upper Hubbard band (UHB). In the LHB of the ground state, two electrons are localized on each U site to form a U⁴⁺(5f⁴) ion, and thus low-energy excitations across the gap are of 5f-5f character. Analogous to conductivity-inducing thermal excitation [6], photoexcitation of UO₂ causes inter-site hopping of 5f electrons, leading to carrier redistribution in the LHB and UHB, formulated as

$$2\text{U}^{4+}(5f^4) \rightarrow \text{U}^{3+}(5f^5) + \text{U}^{5+}(5f^3).$$  (1)
A charge neutral photoexcitation produces a pair of $U^{3+}$ and $U^{5+}$, which, depending on the relative strength between the on-site and nearest-site repulsion, can either form a bound state, such as a Hubbard exciton [7, 8], or remain decoupled. If a lattice deformation is incurred around $U^{3+}$ and $U^{5+}$ by these excitonic states, bound polaron pairs or isolated polarons may form in large or small sizes [6, 9].

In this paper, we present a pump-probe optical reflectivity study of ultrafast dynamics of photoexcited 5f electrons across the Mott gap. Such an investigation has not appeared before to our knowledge, while previous optical studies have been inadequate especially at low temperatures to explore its applications in electronics and photonics. We address ultrafast dynamics including the excitation/relaxation channels and their characteristic timescales, the binding status of $U^{3+}$ and $U^{5+}$, the role of phonons and temperature, and the effect of photoexcitation on electron correlation. We find a long-lived (~1 ns) acoustic phonon in UO$_2$ following photoexcitation, indicating strong electron-phonon coupling. We observe a slow relaxation time of $\sim$2 $\mu$s for photoexcited 5f electrons in the AFM region, and attribute it to the decay process of the Hubbard excitons formed by nearest-neighbor $U^{3+}$-$U^{5+}$ pairs in a background of $U^{4+}$ sites.

2. Experiment

Photoinduced reflectivity measurements were performed using a femtosecond regenerative amplifier producing 6 $\mu$J, 80 fs pulses at 800 nm, at a repetition rate of 250 kHz. The pump pulse at 400 nm (3.1 eV) in our experiments was produced by frequency-doubling of the laser for optical excitation well above the Mott gap. The pump induced change of reflectivity, $\Delta R$, was monitored by the probe pulse at 800 nm as a function of the delay time between pump and probe. The pump fluence ranged from 0.5-70 $\mu$J/cm$^2$, while the typical probe fluence was $\sim$5 times weaker. The fractional changes of reflectivity, $\Delta R/R$, of the probe light reflected from the sample surface were measured by a lock-in amplifier fed by the detected signal from a photodiode. The sample was a 1-mm-thick, (100) surface-oriented single crystal of UO$_2$ and it was mounted in a cryostat for measurements at liquid He temperatures.

3. Results and Discussion

The left panel of Fig. 1 shows the measured reflectivity transients, $\Delta R/R$, of UO$_2$ at several different temperatures (T) as a function of the time delay, $t$, between the pump and probe pulses. Each transient exhibits an initial exponential rise with a time constant, $\tau_{rise}$, followed by a damped oscillation riding on a slow relaxation process. Each transient appears as a negative differential reflectivity, corresponding to photoinduced absorption following excitation.

![Figure 1](image-url)

Fig. 1. Left panel: Measured reflectivity transients of UO$_2$ at different temperatures for a fixed pump fluence 64 $\mu$J/cm$^2$. Smooth lines are exponential fits for the fast relaxation time, $\tau_{fast}$. Right panel:
Extracted temperature dependence of the rise amplitude, $A_0$ (a), risetime, $\tau_{\text{rise}}$ (b), fast relaxation time, $\tau_{\text{fast}}$ (c), and slow relaxation time, $\tau_{\text{slow}}$ (d). The vertical dashed line indicates $T_N = 30.8$ K.

The relaxation can be represented as the sum of two decaying exponentials with respective different relaxation time constants, $\tau_{\text{fast}}$, a fast relaxation time, and $\tau_{\text{slow}}$, a slow relaxation time and a damped oscillation term as in Eq. (2)

$$\Delta R(t)/R = A_0 e^{-t/\tau_{\text{rise}}} + A_{\text{osc}} e^{-t/\tau_{\text{osc}}} \cos(4\pi n v t/\lambda - \delta).$$  \hspace{1cm} (2)

Here $A_{\text{osc}}$ are the component amplitudes, $\tau_{\text{osc}}$ the damping constant of oscillation, $n$ the real refractive index, $\nu$ the sound velocity, $\lambda$ the probe wavelength, and $\delta$ the phase [10]. The right panel of Fig. 1 shows the extracted T-dependence of the rise amplitude, $A_0$, and time constants, $\tau_{\text{rise}}$, $\tau_{\text{fast}}$, and $\tau_{\text{slow}}$, all increasing upon cooling, except for a slight drop in the vicinity of $T_N$ for $\tau_{\text{fast}}$. Remarkably $\tau_{\text{slow}}$ is very long, about 2 $\mu$s at low temperatures, reaching the limitation of measurement with the pulses separated by 4 $\mu$s. By assuming an exponential decay, we calculate $\tau_{\text{slow}}$ from the offsets of $\Delta R/R$ at zero time delay. A long-lived oscillation of $\Delta R/R$ is observed and its frequency of 29.4 GHz is matched to $2n\nu/\lambda$ [11], consistent with an acoustic phonon package (strain pulse) propagating in the sample [10].

The initial quick rise of $\Delta R/R$ originates from the combination of the change of the LHB occupation and the lattice deformation caused by the excitonic states, $U^{3+}$ and $U^{5+}$. The probe pulse at 800 nm accesses the optical transition between the LHB and midgap states momentarily generated by the deformation. The ps rise process includes three steps: electron thermalization, carrier relaxation via optical phonon emission, and the decay of optical to acoustic phonons. If we assume that the pump induced density of midgap states is proportional to the electronic temperature $T_e$, while the initial density is proportional to $T$ (this is based on our measured result that the reflectivity decreases linearly with $T$), the rise amplitude as a function of $T$, $A_0(T)$, of the Mott insulator follows the formalism based on the two-temperature model of a simple metal, written as [12]

$$A_0(T) \propto \sqrt{T^2 + \alpha F - T}.$$  \hspace{1cm} (3)

Here $\alpha$ is a material constant and $F$ is the pump fluence.

Fig. 2. Left panel: Measured reflectivity transients of UO$_2$ at a fixed temperature $T=7$ K for different pump fluences. Smooth lines are exponential fits for the risetimes. Right panel: Extracted pump fluence dependence of the rise and oscillation amplitudes, $A_0$ and $A_{\text{osc}}$, respectively (a), risetime, $\tau_{\text{rise}}$ (b), and slow relaxation time, $\tau_{\text{slow}}$ (c).

From the T-dependence of the characteristic rise and relaxation times, we can derive ultrafast electron and lattice dynamics and perceive electron correlation effects. The $\tau_{\text{rise}}(T)$ can be fitted to the $1/\sqrt{T}$ trend, which describes a hop duration of a polaron [6] and can also be due to longer electron-
lattice thermalization times at low temperatures. The $\tau_{\text{fast}}(T)$ corresponds to the reordering of electron spins after the pump disturbance. Its time scale of 100 ps at T<$T_N$ agrees with earlier identifying of magnetic ordering, though in a different oxide [13]. The observation that $\tau_{\text{fast}}(T)$ shows a drop at $\sim T_N$ and almost disappears at T>$T_N$ supports such magnetic identification. The observed acoustic phonon means lattice distortion present, which likely forms polarons. However, $\tau_{\text{slow}}(T)$ does not follow the exponential function of $1/T$, a characteristic trend for polaron hopping [6], so we exclude the relaxation channel of polaron decay. Instead, we ascribe the slow relaxation time of $\sim 2 \mu$s at T<$T_N$ to the decay of Hubbard excitons formed by nearest-neighbor U^{3+}-U^{5+} pairs. The U^{3+}-U^{5+} pairs form a bound state at T<$T_N$ because of magnetic ordering correlation but quickly recombine at high temperatures because of thermal and spin fluctuations.

The excitation intensity dependence of $\Delta R/R$ at low temperatures helps to reveal the relaxation mechanism, as thermal excitation is negligible when the material is in its ground state. The left panel of Fig. 2 shows the measured reflectivity transients of UO$_2$ at a fixed temperature T=7 K for various pump fluences, $F=0.64-64 \mu$J/cm$^2$, and the extracted amplitudes and time constants are shown in the right panel of Fig. 2. Both $A_0(T)$ in Fig. 1 and $A_0(F)$ in Fig. 2 can be well fitted to Eq. (3), suggesting that our assumption of the density of midgap states is reasonable. The increasing trend of $\tau_{\text{rise}}(F)$ with decreasing $F$ is consistent with a longer time needed for the formation of lattice deformation at low temperatures. The slight variation of $\tau_{\text{slow}}(F)$ with $F$ excludes heating effects. Persistence of oscillations at low pump fluences indicates strong phonon emission due to inter-site photoexcitation.

4. Summary
We have studied the ultrafast dynamics of photoexcited 5f electron in the Mott insulator UO$_2$ using femtosecond pump-probe techniques. An unusually long relaxation time of $\sim 2 \mu$s in the AFM ground state UO$_2$ has been found and ascribed to the decay of Hubbard excitons of photoinduced U^{3+}-U^{5+} pairs. Current work includes detecting photoluminescence from UO$_2$ to confirm the presence of Hubbard excitons and to identify whether the decay is radiative or non-radiative. This work on strongly correlated 5f electrons will project enabling electronic applications for U compounds. In addition, such long-lived excitons in UO$_2$ may make the material a good candidate for the observation of a Bose condensation of excitons, as proposed in Cu$_2$O [7].

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