Coherent energy scale revealed by ultrafast dynamics of UX₃ (X=Al, Sn, Ga) single crystals

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(Dated: May 1, 2014)

Temperature dependence of relaxation dynamics of UX₃ (X = Al, Ga, Sn) compounds is studied using time resolved pump-probe technique in the reflectance geometry. UX₃ is an itinerant antiferromagnet, while UAl₃ and USn₃ are spin fluctuation systems. For UGa₃, our data are consistent with the formation of a spin density wave SDW gap as evidenced from the quasidivergence of the relaxation time τ near the Néel temperature Tₙ. For UAl₃ and USn₃, the relaxation dynamics shows a change from single exponential to two exponential behavior below a particular temperature, suggestive of coherence formation of the 5f electrons with the conduction band electrons. This particular temperature can be attributed to the spin fluctuation temperature Tₘ, a measure of the strength of Kondo coherence. Our Tₘ is consistent with other data such as resistivity and susceptibility measurements. The temperature dependence of the relaxation amplitude and time of UAl₃ and USn₃ were also fitted by the Rothwarf-Taylor model. Our results show ultrafast optical spectroscopy is sensitive to c-f Kondo hybridization in the f-electron systems.

I. INTRODUCTION

The uranium compounds UX₃, where X is a IIIb (Al, Ga, In, Tl) or IVb (Si, Ge, Sn, Pb) element, crystallize in the cubic AuCu₃-type structure and have U-U distances (dₚ₋ₚ) much larger than the Hill limit (∼ 3.5 Å) for uranium compounds. The different degree of hybridization of the 5f electron orbitals with the conduction electron orbitals in these compounds leads to a wide range of magnetic behavior such as Pauli enhanced paramagnetism (UAl₃, USi₃, and UGe₃), antiferromagnetism (UGa₃, UPb₃ and UIn₃), and heavy fermion behavior (USn₃). Due to the the above-mentioned properties and the availability of high quality crystals, UX₃ compounds are ideal candidates for studying how physical properties and underlying electronic structure are related.

The anomalous behavior of the resistivities of UX₃ compounds can be explained on the basis of spin fluctuations in narrow 5f bands. A temperature characteristic of the spin fluctuations in the UX₃ compounds is the spin fluctuation temperature, Tₘ, which expresses the strength of hybridization between f and conduction electrons (c-f hybridization). The degree of hybridization is related to the degree of delocalization of the f-electrons. A high value of Tₘ corresponds to more easily hybridized (delocalized) electrons. Above Tₘ, f-electrons are localized; whereas below Tₘ, there is quasiparticle coherence from the hybridization between f-electrons and conduction electrons, i.e., f-electrons now become more delocalized (or itinerant). The effective hybridization below Tₘ leads to changes in measured physical properties. For example, the electrical resistivity changes from a T-linear law above Tₘ to a T-quadratic law below this temperature. The temperature at which the magnetic susceptibility reaches a Curie-Weiss law is theoretically of the order of Tₘ. A modified Curie-Weiss law, i.e., χ(T) = χ₀ + C/(T + T*), associates T* with Tₘ for relatively strong c-f hybridization.

Ultrafast time-resolved pump-probe spectroscopy has been recognized as a powerful technique to study the nonequilibrium carrier dynamics in strongly correlated electron materials. In addition to distinguishing different phases in a material by their different relaxation dynamics, it can discern whether one phase coexists or competes with another phase in close proximity, giving information on the nature of low energy electronic structure of correlated electron systems, for example, in high-temperature superconductors. Pump-probe experiments have also been performed on actinide compounds, such as the itinerant antiferromagnets UNiGa₃ and U₃Pt₃, and the heavy-fermion superconductor PuCoGa₅.

The hybridization between the conduction electrons and the localized f electrons also causes a narrow gap to form in the density of states near the Fermi level. This gap, called the hybridization gap, results in a relaxation bottleneck, evidenced by an increase in the relaxation time τ at low temperatures. For example, in heavy fermions such as YbAgCu₄ and SnB₆, τ increases monotonically with decreasing temperature. The temperature dependence of the relaxation amplitude and time were fit using the Rothwarf-Taylor model. In this paper, we investigate the ultrafast dynamics in three isostructural uranium compounds, UAl₃, UGa₃, and USn₃, using the ultrafast pump-probe technique. The variation in hybridization strength is responsible for the differences in properties of these three isostructural compounds. UAl₃ and USn₃ are categorized as spin-fluctuation systems. UGa₃ does not behave as a spin fluctuation system, but is an itinerant 5f electron antiferromagnet. In fitting the transient change in reflectivity for UAl₃ and USn₃, we needed a two-exponential decay function below Tₘ, which points to the presence of
two relaxation channels below $T_{sf}$. This arises from the hybridization between $f$ electrons and conduction electrons below $T_{sf}$. This shows that the ultrafast pump probe technique is sensitive to $c$-$f$ hybridization in $f$-electron systems. Our $T_{sf}$ is consistent with that obtained from resistivity and susceptibility measurements. We were also able to fit the temperature dependence of the relaxation amplitude and time using the RT model. For UGa$_3$, the relaxation time diverges as the temperature approaches the Néel temperature $T_N$, corresponding to the formation of a spin density wave (SDW) gap near the Fermi level.

![Graph](image)

**FIG. 1:** Transient reflection $\Delta R/R$ versus pump-probe time delay at different temperatures for (a) UAl$_3$, and (b) USn$_3$. Thick solid curves denote exponential fits of data.

**III. UAl$_3$ AND USn$_3$**

In Fig. 2, we show the $\Delta R/R$ at different temperatures for (a) UAl$_3$ and (b) USn$_3$, as a function of the time delay between the pump and probe pulses. In both UAl$_3$ and USn$_3$, only a fast relaxation of $\sim$500 fs, which is typical of regular metals, is observed at high temperatures. At low temperatures, an additional slow, positive picosecond relaxation is observed. Data at low temperatures are fit-
particular crossover temperature — a change from one- to two-exponential decay occurs at a supercritical temperature measurements (∼ 50 K for USn₃, suggestive of two relaxation channels below this crossover temperature. These crossover temperatures are of the order of the spin fluctuation temperatures \( T_{sf} \) obtained in these compounds from temperature-dependent electrical resistivity and magnetic susceptibility measurements (∼150 K for UAl₃ and ∼50 K for USn₃). We thus associate this crossover temperature to the spin fluctuation temperature \( T_{sf} \).

To understand the different characteristic temperatures in UAl₃ and USn₃, we have also performed band structure calculations in the framework of the density functional theory, by using the WIEN2k linearized augmented plane wave method. A generalized gradient approximation was used to treat exchange and correlation. Spin-orbit coupling was included in a second-variational way. The obtained U partial 5f density of states, as shown in Fig. 4, indicates a narrower peak width near the Fermi energy \( (E=0) \) in USn₃ compared to UAl₃. view of the fact that the spin-orbit coupling is quite local to the U atoms, one would expect the same effect on both USn₃ and UAl₃. A reasonable explanation for this difference is a smaller hybridization gap in USn₃ compared to UAl₃, due to the weakening of the hybridization in USn₃ — a result of the lattice expansion \( (a=4.626 \, \text{Å in USn₃ versus } a=4.264 \, \text{Å in UAl₃}) \). Though conventional band structure calculations underestimate the correlation effect, the trend of smaller coherence energy scale in USn₃ than in UAl₃ should be robust, as has recently been exemplified in other isostructural actinide compounds.

In this context, the two-exponential behavior at low temperature can be explained by the c-f hybridization occurring below \( T_{sf} \). Below \( T_{sf} \), the interaction of partially-filled f shell electrons with conduction electrons lead to the formation of heavy quasiparticles. As the f-electrons are localized above \( T_{sf} \), relaxation occurs through phonon channel only. Hence only a single exponential decay is expected above \( T_{sf} \). When \( T < T_{sf} \), the spin fluctuation channel opens up due to hybridization. Electrons now relax via both phonon and spin fluctuation channels resulting in a two-exponential decay behavior. Also, a higher \( T_{sf} \) value in UAl₃ compared to USn₃ points to a stronger c-f hybridization, which is expected, as c-f hybridization tends to decrease as the size of the non-f atom increases, which causes the lattice expansion as we discussed above.

The hybridization between the conduction band and the localized f-levels also results in the formation of a narrow gap in the density of states near the Fermi level, called the hybridization gap. The presence of this gap causes a bottleneck in quasiparticle relaxation, resulting in a divergence of the relaxation time at low temperatures. The temperature dependence of the relaxation amplitude and relaxation time can be quantitively explained by the Rothwarf-Taylor (RT) model. It is a phenomenological model that was used to describe the re-

![FIG. 4: Total DOS calculated from the LAPW method for UAl3 and USn3, in the magnetic unit cell, in the energy range (-2,2) eV. Note the narrower peak width near the Fermi energy (E=0) in USn3 compared to UAl3.](image-url)
The pump-probe technique is sensitive to the hybridization of the heavy-fermion metals,\textsuperscript{14,16} itinerant antiferromagnets,\textsuperscript{14,16} and heavy-fermion metals,\textsuperscript{15} where the presence of a gap in the electronic density of states gives rise to a relaxation bottleneck for carrier relaxation. In heavy fermions, after the initial photo-excitation by a pump pulse, the subsequent fast relaxation due to electron-electron scattering results in excess densities of electron-hole pairs (EHPs) and high-frequency phonons (HFPs). When an EHP with energy $\geq \Delta$ ($\Delta$ = hybridization gap) recombines, a HFP is created. The HFPs released in the EHP recombination are trapped within the excited volume and can re-excite EHPs; hence they act as a bottleneck for EHP recombination, and recovery is governed by the decay of the HFP population. The evolution of EHP and HFP populations is described by a set of two coupled nonlinear differential equations.

The results of the RT model are as follows:\textsuperscript{17,33} from the amplitude $A(T)$, one obtains the density of thermally excited EHPs $n_T$ via the relation

$$n_T(T) \propto A(T)^{-1} - 1$$

(1)

where $A(T)$ is the normalized amplitude ($A(T) = A(T)/A(T \to 0)$). Then we fit the experimental $n_T(T)$ to the expression:\textsuperscript{17}

$$n_T(T) \propto \sqrt{T} \exp(-\Delta/T),$$

(2)

where the hybridization gap $\Delta$ is temperature independent (or very weakly temperature dependent) and can be obtained from the fitting. Moreover, for a constant pump intensity, the temperature-dependence of $n_T$ also governs the temperature-dependence of $\tau^{-1}$, given by

$$\tau^{-1}(T) = \Gamma[\delta(\beta n_T + 1)^{-1} + 2n_T(\Delta + \alpha T\Delta^4)]$$

(3)

where $\Gamma$, $\delta$, $\beta$ and $\alpha$ are $T$-independent fitting parameters.

Since, below $T_{sf}$, the second relaxation component appears, we attribute it to relaxation across the hybridization gap, and use the RT model to fit the its amplitude and relaxation time below $T_{sf}$ in UAl$_3$ and USn$_3$. The inset of Fig. 2(a) shows $n_T(T)$ obtained from $A_{\text{slow}}(T)$ using Eq. 1, with the solid line being the fit to Eq. 2, with the fitting parameter $\Delta \approx (230 \pm 10) \text{ K}$. The fitted values of $n_T(T)$ are then inserted into Eq. 3 to fit the experimental values of $\tau_{\text{slow}}(T)$, shown in Fig. 2(b). Similar fits are also done for USn$_3$, as shown in Fig. 3 yielding $\Delta \approx (90 \pm 20) \text{ K}$. The good fits show that the slow relaxation component in both UAl$_3$ and USn$_3$ can be described by assuming EHPs relaxing across the hybridization gap near the Fermi surface. More interestingly, the extracted hybridization gap in UAl$_3$ is larger than in USn$_3$, in qualitative agreement with the band structure results. This comparison of hybridization gap is also consistent with that of spin fluctuation energy scale $T_{sf}$ discussed above. Our results show that the ultrafast pump-probe technique is sensitive to the hybridization of $f$-electron orbitals with the conduction electron orbitals.

**FIG. 5:** (a) Photoinduced change in reflectivity $\Delta R/R$ versus pump-probe time delay at different temperatures of UGa$_3$. Thick blue (cyan) curves denote one-exponential fits of data at $T\approx 40 \text{ K}$ (48 K). Temperature dependence of (b) amplitude and (c) relaxation time for UGa$_3$ obtained from one-exponential fits, with dashed lines in (b) and (c) being fits to the RT model from 40 K to $T_N$.

**IV. UGa$_3$**

We now turn to the relaxation dynamics of UGa$_3$. UGa$_3$ is not a spin fluctuation system — it is a SDW system with Néel temperature $T_N=65 \text{ K}$. It is a moderate heavy fermion with Sommerfeld coefficient 52 mJ/K$^2$mol\textsuperscript{34} and is reported to follow a modified Curie-Weiss law behavior\textsuperscript{35} with $T^* = 2080 \text{ K}$ which is in-
dicative of strong hybridization in this compound. The 5f electrons in UGa₃ can be considered itinerant because of the large hybridization of 5f orbitals with conduction electron orbitals. The photoinduced change in reflectivity, as shown in Fig. 5(a), can be fitted with a single exponential decay \( \Delta R/R(t) = A(T) \exp(-t/\tau) \). The extracted relaxation amplitude \( A(T) \) and time \( \tau(T) \) are shown in Fig. 5(b) and Fig. 5(c), respectively. Upon entering the SDW phase, \( A(T) \) increases with decreasing temperature. However, instead of monotonically increasing as in UAl₃ and USn₃, \( A(T) \) now attains a maximum at \( \sim 40 \) K and starts decreasing with decreasing temperature (see Fig. 5(b)). Concurrently, \( \tau \) exhibits a quasi-divergence at \( T_N \), consistent with that observed in itinerant antiferromagnets UNiGa₅ and UPtGa₅, where the opening up of the SDW gap causes a bottleneck in quasiparticle relaxation. In contrast to UNiGa₅ and UPtGa₅, however, where \( \tau \) increases with decreasing temperature at low temperatures, \( \tau \) in UGa₃ shows a (1) shoulder (or change in curvature) at 40 K, and (2) decrease with decreasing temperature. An anomaly at a spin-reorientation temperature \( T_{sr} = 40 \) K has been reported in other measurements of UGa₃, whether in the presence of a magnetic field (nuclear magnetic resonance, neutron scattering, magnetic susceptibility) or in the absence of a magnetic field (thermal conductivity and neutron scattering). This anomaly has been associated with a reorientation of the ordered magnetic moments, which induces strong modifications of the uranium 5f orbitals. The fact that the transition is observed in the absence of a magnetic field is an indication that the bump we see at 40 K in our pump probe measurement is not an artifact, but corresponds to the moment re-orientation as has been reported in other measurements mentioned above.

We use the model proposed by Kabanov et al. to analyze the temperature dependence of \( A \). The temperature dependence of the relaxation amplitude in the SDW state for an isotropic temperature-dependent gap \( \Delta_{SDW}(T) \) is given by (writing \( \Delta_{SDW}(T) \) as \( \Delta(T) \))

\[
A(T) = \frac{\epsilon_I/(\Delta(T) + k_B T/2)}{1 + \zeta \sqrt{\frac{2k_B T}{\pi \Delta(T)}} \exp[-\Delta(T)/k_B T]},
\]

where \( \epsilon_I \) the pump laser intensity per unit cell, \( \zeta \) is a constant, and \( \Delta(T) \) obeys a weak-coupling BCS temperature dependence. The above expression for \( A(T) \) describes a reduction in the photoexcited quasiparticle density with increase in temperature, due to the decrease in gap energy and corresponding enhanced phonon emission during the initial relaxation. A good fit between the experimental \( A(T) \) and Eq. (4) can only be made from \( T_N \) down to \( \sim 40 \) K, where \( T_N = 55 \) K is a fitting parameter. In the SDW state (\( T < T_N \)), the temperature-dependence of \( \tau \) can be obtained from Eq. (4), but can be written in the alternative form (writing \( \Delta_{SDW}(T) \) as \( \Delta(T) \))

\[
\tau^{-1}(T) = \Gamma[\delta A(T) + \eta \sqrt{\Delta(T) T \exp[-\Delta(T)/T]}] \times \left[ \Delta(T) + \alpha T \Delta(T)^4 \right].
\]

The fit of \( \tau(T) \) to Eq. (5) is shown in Fig. 5(c). Once again, a good fit is obtained only from \( T_N \) to \( \sim 30 \) K, close to \( T_{sr} \). Below \( T_{sr} \), the fit deviates from the experimental data, consistent with the existence of another transition at \( T_{sr} \).

V. CONCLUSION

We have performed time-resolved photoinduced change in reflectivity measurements on three isostructural uranium compounds — UAl₃, UGa₃ and USn₃. The values of \( T_{sf} \), a measure of the degree of hybridization, in UAl₃ and USn₃, are consistent with data from other measurements. Our fit of the slow component to the Rothwarf-Taylor model shows that the slow component can be described by assuming electron-hole pairs relaxing across the hybridization gap. We have thus shown the pump probe technique to be sensitive to c-f hybridization. Our data on UGa₃ is consistent with the formation of a SDW gap at \( T_N = 60 \) K, and a reorientation of magnetic moments at \( T_{sr} = 40 \) K.

VI. ACKNOWLEDGEMENTS

E.E.M.C. acknowledges support from G. T. Seaborg Postdoctoral Fellowship, the Singapore Ministry of Education Academic Research Fund Tier 2 (ARC23/08), as well as the National Research Foundation Competitive Research Programme (NRF-CRP4-2008-04). Work at Los Alamos was supported by the U.S. DOE at LANL under Contract No. DE-AC52-06NA25396, the U.S. DOE Office of Basic Energy Sciences, and the LDRD Program at LANL. The electronic structure calculations were performed on a computer cluster at the Center for Integrated Nanotechnologies, a U.S. DOE Office of Basic Energy Sciences user facility.

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