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

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The temperature dependence of relaxation dynamics of UX₃ (X = Al, Ga, Sn) compounds is studied using the time-resolved pump-probe technique in reflectance geometry. For UGa₃, our data are consistent with the formation of a spin density wave gap as evidenced from the quasidivergence of the relaxation time τ near the Néel temperature T_N. 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 T_{sf}, a measure of the strength of Kondo coherence. Our T_{sf} 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 that ultrafast optical spectroscopy is sensitive to c-f Kondo hybridization in the f-electron systems.

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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 (d(U,U)) much larger than the Hill limit (~3.5 Å) for uranium compounds. 2 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 UN₃), and heavy-fermion behavior (USn₃). 1,3,4 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. 5,6 A temperature characteristic of the spin fluctuations in the UX₃ compounds is the spin fluctuation temperature T_{sf}, 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 T_{sf} corresponds to more easily hybridized (delocalized) electrons. Above T_{sf}, f electrons are localized, whereas below T_{sf}, 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 T_{sf} leads to changes in measured physical properties. For example, the electrical resistivity changes from a T-linear law above T_{sf} to a T-quadratic law below this temperature. 6-9 The temperature at which the magnetic susceptibility reaches a Curie-Weiss law is theoretically of the order of T_{sf}; 6 A modified Curie-Weiss law, i.e., χ(T) = χ₀ + C/(T + T°), associates T° with T_{sf} for relatively strong c-f hybridization. 10,11

Ultrafast time-resolved pump-probe spectroscopy has been recognized as a powerful technique to study the nonequilibrium uranium 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, 12-14 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 UPtGa₃, 15,16 and the heavy-fermion superconductor PuCoGa₅. 17

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. 18 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 SmB₆, τ increases monotonically with decreasing temperature. 18 The temperature dependence of the relaxation amplitude and time were fitted using the Rothwarf-Taylor (RT) model. In this paper, we investigate the ultrafast dynamics in three isostructural uranium compounds, UAl₃, UGe₃, 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. 7,19-23 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 T_{sf}, 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 UGa₃, 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.

II. EXPERIMENTAL SETUP

In our pump-probe experimental setup in reflectance geometry, a Ti:sapphire laser producing sub-100 fs pulses at $\approx 800$ nm (1.55 eV) was used as a source of both pump and probe pulses. The pump and probe pulses were cross polarized. The pump spot diameter was 60 $\mu$m and that of the probe was 30 $\mu$m. The reflected probe beam was focused onto an avalanche photodiode detector. The photoinduced change in reflectivity ($\Delta R/R$) was measured using lock-in detection. In order to minimize noise, the pump beam was modulated at 100 kHz with an acousto-optical modulator. The experiments were performed with an average pump power of 2 mW, giving a pump fluence of $\sim 1 \mu J/cm^2$. The probe intensity was approximately ten times lower. Data were taken from 10 K to 300 K. The experiments were performed on single crystals of UX$_3$ ($X = Al, Ga, Sn$) grown using the standard flux technique, with X used as the flux in each case.23

III. UAI$_3$ AND USN$_3$

In Fig. 1 we show the $\Delta R/R$ at different temperatures for (a) UAI$_3$ and (b) USN$_3$, as a function of the time delay between the pump and probe pulses. In both UAI$_3$ 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 fitted to the two-exponential decay function $\Delta R/R(t) = A_{\text{fast}}(T) \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}}(T) \exp(-t/\tau_{\text{slow}})$. This change from one- to two-exponential decay occurs at a particular crossover temperature, $\sim 200$ K for UAI$_3$ and $\sim 50$ K for USN$_3$, 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 ($\sim 150$ K for UAI$_3$ and $\sim 50$ K for USN$_3$). We thus associate this crossover temperature with the spin fluctuation temperature $T_{sf}$.

To understand the different characteristic temperatures in UAI$_3$ and USN$_3$, we have also performed band structure calculations in the framework of the density functional theory, by using the WIEN2k linearized augmented plane wave method.27 A generalized gradient approximation28 was used to treat exchange and correlation. Spin-orbit coupling was included in a second-variational way. The obtained U partial density of states, as shown in Fig. 2, indicates a narrower peak width near the Fermi energy, in USN$_3$ as compared with UAI$_3$. In addition, one can see that the splitting between the two major peaks is smaller in USN$_3$ than in UAI$_3$. In view of the fact that the spin-orbit coupling is quite local to the U atoms, one would expect the same effect on both USN$_3$ and UAI$_3$. A possible explanation for this difference is a smaller hybridization gap in USN$_3$ compared to UAI$_3$, due to the weakening of the hybridization in USN$_3$, a result of the

lattice expansion ($a = 4.626$ Å in USN$_3$ versus $a = 4.264$ Å in UAI$_3$).24 Though conventional band structure calculations underestimate the correlation effect, the trend of smaller coherence energy scale in USN$_3$ than in UAI$_3$ should be robust, as has recently been exemplified in other isostructural actinide compounds.29

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 leads to the formation of heavy quasiparticles.30 As the $f$ electrons are localized above $T_{sf}$, relaxation occurs through phonon channels 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 UAI$_3$ compared to USN$_3$ 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 quantitatively explained by the Rothwarf-Taylor (RT) model. It is a phenomenological model that was used to describe the relaxation of photoexcited superconductors, and itinerant antiferromagnets, and heavy-fermion metals, 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 $\Delta$ (where $\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: From the experimental values of $\tau_{\text{slow}}(T)$ obtained from $A_{\text{slow}}(T)$ using Eq. (1), with the solid line being the fit to Eq. (2), with the fitting parameter $\Delta \approx (230 \pm 10)$ 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. 3(b). Similar fits are also done for USn3, as shown in Fig. 4, yielding $\Delta \approx (90 \pm 20)$ K. The good fits show that the slow relaxation component in both UAl3 and USn3 can be described by assuming EHPs relaxing across the hybridization gap near the Fermi surface. More interestingly, the extracted hybridization gap in UAl3 is larger than in USn3, in qualitative agreement with the band structure results. This comparison of the 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. 2. (Color online) Uranium $5f$ partial 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.

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. 3(b). Similar fits are also done for USn3, as shown in Fig. 4, yielding $\Delta \approx (90 \pm 20)$ K. The good fits show that the slow relaxation component in both UAl3 and USn3 can be described by assuming EHPs relaxing across the hybridization gap near the Fermi surface. More interestingly, the extracted hybridization gap in UAl3 is larger than in USn3, in qualitative agreement with the band structure results. This comparison of the 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. 3. Temperature dependence of (a) amplitudes and (b) relaxation times for UAl3. Solid lines are fits to the RT model of the slow component. The shaded regions represent the temperature region above $T_{sf}$ where, though a two-exponential fit is better, a one-exponential fit suffices.

dependence of $\tau^{-1}$, given by

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

where $\Gamma$, $\delta$, $\beta$, and $\alpha$ are $T$-independent fitting parameters. We note that the same type of RT analysis can be made for the quasiparticle scattering off spin fluctuations, when the latter have a spin resonance nature at a finite frequency. Under this condition, spin fluctuations will exhibit a gaplike feature in the integrated spin spectral function.

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 amplitude and relaxation time below $T_{sf}$ in UAl3 and USn3. The inset of Fig. 3(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 $\Delta \approx (230 \pm 10)$ 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. 3(b). Similar fits are also done for USn3, as shown in Fig. 4, yielding $\Delta \approx (90 \pm 20)$ K. The good fits show that the slow relaxation component in both UAl3 and USn3 can be described by assuming EHPs relaxing across the hybridization gap near the Fermi surface. More interestingly, the extracted hybridization gap in UAl3 is larger than in USn3, in qualitative agreement with the band structure results. This comparison of the 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.
region above $T_{sf}$ the slow component. The shaded regions represent the temperature relaxation time for USn3. Solid lines are fits to the RT model of other heavy fermions.18

susceptibility maximum at some crossover temperature ($T_{sf}$) being a crossover temperature, rather than a sharp change in $A$ with $T_{sf}$, is consistent with that seen in other heavy fermions.18

It is worth mentioning that mixed-valence systems exhibit the same behavior as spin fluctuation systems by having a susceptibility maximum at some crossover temperature ($T_{sf}$) in spin fluctuation and $T_{max}$ in mixed valence). However, the sign of magnetoresistivity (MR) is opposite—negative in spin fluctuation systems and positive in mixed-valence systems. For example, in UCoGa3, a normal positive behavior in spin fluctuation systems and positive in mixed-valence $\Delta \rho / \rho$ and spin-orbit sum rule analysis showed that the 5$f$ states of $\alpha$-U metal and US are largely itinerant, those in USe are localized to a greater extent, whereas those in UTe are almost entirely localized.38 Electron energy-loss spectroscopy and spin-orbit sum rule analysis showed that the 5$f$ states in URu$_2$Si$_2$ are moderately localized, though not as much as USe and UTe.38 However, electronic structure calculation of URu$_2$Si$_2$ showed that a completely itinerant picture is sufficient to provide an excellent explanation of the low-temperature data of the paramagnetic and antiferromagnetic phases.39,40 The itinerant band picture is adequate for the monocarbide UC, and acceptable for the mononitride UN.41 Furthermore, we note that the fast component of dynamics has a very different temperature dependence of relaxation between UAl3 and USn3 [compare Figs. 3(b) and 4(b)]. Since this energy scale (1/\tau_{fast}) is larger than that involved in the slow dynamics, the understanding of the fast dynamics may help identify the relevance of spin fluctuations, mixed valence, and dual nature in these heavy-fermion systems; how these different descriptions can explain the crossover from a single-to double-exponential relaxation behavior in our pump-probe data requires further theoretical and experimental work.

IV. UGa3

We now turn to the relaxation dynamics of UGa3. UGa3 is not a spin fluctuation system; it is a SDW system with Néel temperature $T_N = 65$ K. It is a moderate heavy fermion with Sommerfeld coefficient 52 mJ/K$^2$·mol,19 and is reported to follow a modified Curie-Weiss law behavior $42$ with $T^* = 2080$ K which is indicative of strong hybridization in this compound. The 5$f$ electrons in UGa3 can be considered itinerant because of the large hybridization of 5$f$ orbitals with conduction electron orbitals. Neutron scattering and resistivity data revealed an antiferromagnetic transition at $\sim$70 K. Kaczorowski42 summarized the properties of UGa3 and found it to fulfill all the main criteria for itinerant magnetism. Further evidence for the itinerancy of 5$f$ electrons in UGa3 comes from data of angular correlation of the electron-positron annihilation radiation and is supported by electronic structure calculations within the local density approximation.27,45

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 Figs. 5(b) and 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 ≈40 K and starts decreasing with decreasing temperature [see Fig. 5(b)]. Concurrently, τ exhibits a quasidivergence at $T_N$, consistent with that observed in itinerant antiferromagnets UNiGa$_5$ and UPtGa$_5$, where the opening up of the SDW gap causes a bottleneck in quasiparticle relaxation. In contrast to UNiGa$_5$ and UPtGa$_5$, however, where τ increases with decreasing temperature at low temperatures, τ in UGa$_3$ 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 UGa$_3$, whether in the presence of a magnetic field (nuclear magnetic resonance, neutron scattering, magnetic susceptibility, Mössbauer)), 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 5$f$ orbitals. The magnetic moments, oriented along the [110] axis below 40 K, reorient into the [111] direction at 40 K. The fact that the transition is observed in the absence of 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 reorientation 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 is given by

$$A(T) = \frac{\epsilon_l}{[\Delta(T) + k_BT/2]} \quad \text{[writing } \Delta_{SDW}(T) \text{ as } \Delta(T)]$$

where $\epsilon_l$ is the pump laser intensity per unit cell, $\xi$ 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 ~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. (3), but can be written in the alternative form [writing $\Delta_{SDW}(T)$ as $\Delta(T)$]

$$\tau^{-1}(T) = \Gamma'[\Delta(T) + \eta \sqrt{\Delta(T)} \exp[-\Delta(T)/T]] \times [\Delta(T) + \alpha T \Delta(T)^{4/3}].$$

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 ~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—UAl$_3$, UGa$_3$, and USn$_3$. The values of $T_{sf}$, a measure of the degree of hybridization, in UAl$_3$ and USn$_3$ 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 magnetic moments at $T_{sr} = 40$ K.

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