Abstract

We present the first femtosecond studies of electron-phonon (e-ph) thermalization in heavy fermion compounds. The e-ph thermalization time $\tau_{ep}$ increases below the Kondo temperature by more than two orders of magnitude as $T = 0$ K is approached. Analysis using the two-temperature model and numerical simulations based on Boltzmann’s equations suggest that this anomalous slowing down of the e-ph thermalization derives from the large electronic specific heat and the suppression of scattering between heavy electrons and phonons.
Recent experiments have demonstrated that femtosecond time-resolved optical spectroscopy is a sensitive tool to probe the low energy electronic structure of strongly correlated electron systems[1-4], complementing conventional time-averaged frequency-domain methods. In these experiments, a femtosecond laser pulse excites a non-thermal electron distribution. This non-thermal distribution rapidly thermalizes through electron-electron (e-e) interactions resulting in a change in the occupied density of states (DOS) in proximity to the Fermi energy ($E_f$). Therefore, by measuring photoinduced reflectivity or transmissivity dynamics as a function of temperature ($T$), it is possible to sensitively probe the nature of the electronic ground state. For example, femtosecond measurements of the carrier relaxation dynamics of high-$T_c$ superconductors and charge density wave compounds have provided new insights into the low energy electronic structure of these materials [1-3]. What is particularly important is that even though the probe photon wavelength in these experiments ranges from the far-infrared [3], the near-IR [1], up to several eV [4], the relaxation dynamics on identical samples is the same [3], supporting the basic idea [1] that dynamic photoinduced reflectivity measurements, in many instances, probe relaxation and recombination processes of quasiparticles in the vicinity of $E_f$.

In this Letter, we present the first studies of carrier relaxation dynamics in heavy fermion (HF) compounds using femtosecond time-resolved optical spectroscopy, aiming to elucidate the effect of localized $f$-electrons [5] on the quasiparticle relaxation dynamics. We have measured the time-resolved photoinduced reflectivity $\Delta R/R$ dynamics as a function of temperature on the series of HF compounds Yb$X$Cu$_4$ ($X$=Ag, Cd, In) [6] in comparison to their non-magnetic counterparts Lu$X$Cu$_4$. Our results reveal that the carrier relaxation dynamics are extremely sensitive to the low energy DOS near $E_F$. In particular, in HF compounds the relaxation time $\tau_r$ shows a hundred-fold increase between the Kondo temperature ($T_K$) and 10 K, while in the non-magnetic analogues $\tau_r$ is nearly constant, similar to conventional metals like Ag, Au, and Cu [7]. Our analysis shows that the relaxation dynamics can be attributed to e-ph thermalization, and that the anomalous slowing down of the e-ph thermalization stems from the large electronic specific heat in HF compounds and suppression of e-ph scattering within the peak in the enhanced density of states near $E_f$.

In the following, we focus on YbAgCu$_4$ (a prototypical HF system with $T_K \sim 100$ K and low temperature Sommerfeld coefficient $\gamma \sim 210$ mJ/mol K$^2$) [6] compared to its non-magnetic counterpart LuAgCu$_4$ ($\gamma \sim 10$ mJ/mol K$^2$). The experiments were performed
on freshly polished flux-grown single crystals. We used a standard pump-probe set-up with a mode-locked Ti:Sapphire laser producing 20 fs pulses centered at 800 nm (photon energy $\hbar \omega_{ph} \approx 1.5$ eV) with an 80 MHz repetition rate. The photoinduced (PI) changes in reflectivity $\Delta R/R$ were measured using a photodiode and lock-in detection. The pump fluence was kept below 0.1 $\mu$J/cm$^2$ to minimize the overall heating of the illuminated spot, while the pump/probe intensity ratio was $\sim 30$. Steady-state heating effects were accounted for as described in [11], yielding an uncertainty in temperature of $\pm 3$ K (in all the data the temperature increase of the illuminated spot has been accounted for).

Figure 1 presents the PI reflectivity traces on the two compounds at several temperatures between $\approx 10$ K and 300 K. The relaxation dynamics of the non-HF compound LuAgCu$_4$ display a very weak temperature dependence, with $\Delta R/R$ recovering on a sub-picosecond timescale at all T. The dynamics are similar to regular metals such as Au and Ag [7], where the recovery is predominantly due to e-ph thermalization. In contrast, Fig. 1(b) shows that for YbAgCu, the quasiparticle dynamics are strongly $T$-dependent. Specifically, above $\sim 140$ K, the recovery time $\tau_r$ (determined by a $\exp(-t/\tau_r)$ fit to the data) is virtually $T$-independent but increases by more than two orders of magnitude as $T \to 0$ K. We have measured similar dynamics on YbCdCu$_4$ ($T_K \sim 100$ K, $\gamma \sim 200$ mJ/mol K$^2$). Furthermore, a similar divergence of $\tau_r$ occurs for CeCoIn$_5$ below $\approx 60$ K, implying that the observed increase in the relaxation time starting at $\sim T_K$ and its subsequent divergence as $T \to 0$ K is a generic feature of HF compounds and derives from their low energy electronic structure.

The rise-time dynamics are also different in the two compounds. For LuAgCu$_4$, the rise-time is $\sim 100$ fs at all temperatures. This is again similar to what has been measured on conventional metals and reflects the time it takes for the initially created high energy quasiparticles to thermalize towards $E_f$. Above $\sim 25$ K, YbAgCu$_4$ displays a similar (fast) rise-time. Below this temperature the rise-time increases and, as the semi-log plot in Fig. 1(b) reveals, becomes two-exponential at the lowest temperatures. Similar behavior also occurs for CeCoIn$_5$, but is absent in YbCdCu$_4$ indicating a strong dependence on the details of the low energy electronic structure in HF compounds. While noting the presence of these anomalous rise-time dynamics, further systematic studies are needed to obtain a more complete understanding. In the following, we focus on the anomalous temperature dependence of recovery dynamics below $T_K$ which seem to be a general feature of HF compounds.
In conventional metals, the initial photoinduced change in the reflectivity arises from changes in occupation near \(E_f\) after e-e thermalization. Subsequently, the PI reflectivity recovery dynamics proceed on a picosecond timescale governed by e-ph thermalization\[7\]. The two temperature model (TTM) serves as a useful starting point in describing e-ph thermalization in metals.\[8, 10\]. The TTM describes the time evolution of the electron \((T_e)\) and lattice \((T_l)\) temperatures by two coupled differential equations\[7, 8\]. In the low photoexcitation energy density limit, as in our case, when \(T_e - T_l \ll T_l\) over the entire temperature range, the set of two coupled differential equations can be linearized resulting in the following expression for the e-ph thermalization time

\[
\tau_{ep}^{-1} = g(C_e^{-1} + C_l^{-1}) .
\]  

Here \(C_e\) and \(C_l\) are the electronic and lattice specific heats, respectively, and \(g(T_l)\) is the e-ph coupling function. In the case of simple metals, when the electron bandwidth is much larger than the Debye energy \(\hbar \omega_D = k_B \Theta_D\), and using the Debye model for the e-ph interaction, \(g(T)\) has particularly simple form. It is given by \(g(T) = dG(T)/dT\), where

\[
G(T) = 4g_\infty \left(\frac{T}{\Theta_D}\right)^5 \int_0^{\Theta_D/T} dx x^4 e^{x - 1} \chi(x, T). 
\]  

Here \(g_\infty\) is termed the e-ph coupling constant, while \(\chi(x, T)\) is included to account for the variation in the electronic DOS, \(D_e(\epsilon)\), and the normalized e-ph scattering strength \(F(\epsilon, \epsilon')\), over the energy range \(E_f \pm \hbar \omega_D\). It can be shown using Fermi’s golden rule that

\[
\chi(x, T) = \frac{1}{\xi} \int_{-\infty}^{\infty} d\epsilon \frac{D_e(\epsilon) D_e(\epsilon')}{D_0^2} \{f_0(\epsilon) - f_0(\epsilon')\},
\]  

where \(\epsilon' = \epsilon + \xi\), and \(\xi = xT\) and \(f_0\) is the Fermi-Dirac distribution. In metals like Au or Ag, \(D_{el}(\epsilon)\) and \(F\) are approximately constant in this energy range, i.e. \(D_e(\epsilon) = D_0\) and \(F = 1\), giving \(\chi \equiv 1\). \(g_\infty\) is typically \(10^{15} - 10^{16}\) W/mol K (e.g. for Cu \(g_\infty = 6.2 \times 10^{15}\) W/mol K corresponding to \(g(300K) = 1 \times 10^{17}\) W/m³K\[13\]).

At high temperatures \((T > \Theta_D)\), \(\tau_{ep}(T)\) given by the TTM has been found to describe the temperature as well as photoexcitation intensity dependence of measured \(\tau_r(T)\)\[7, 13\]. Moreover, since the absolute value of \(\tau_{ep}\) is determined by a single parameter \(g_\infty\), the technique has been successfully used to determine the dimensionless e-ph coupling constants \(\lambda\) in superconductors\[10, 14\]. However, at low temperatures \((T \lesssim \Theta_D/5)\) the TTM prediction
of $\tau_{ep} \propto T^{-3}$ has never been observed in metals - instead, at low temperatures $\tau_r$ saturates at a constant value. The discrepancy between the experimental results and the TTM was found to be due to the fact that the TTM neglects e-e thermalization processes (by implicitly assuming that a Fermi-Dirac distribution is created instantly following photoexcitation). From simulations using coupled Boltzmann equations, Groeneveld et al. showed that this discrepancy is due to the fact that at low temperatures the e-e and e-ph thermalization times are comparable. Since $\tau_{ep} \propto T$ above $\approx \Theta_D/6$, while $\tau_{ee} \propto T^{-2}$ - see Eq.(16) of Ref.[7], the TTM is expected to fail at low temperatures where $\tau_{ee} \geq \tau_{ep}$.

In Fig.2 we plot the T-dependence of $\tau_r$ on LuAgCu$_4$ (solid circles), together with the TTM prediction for $\tau_{ep}$ (dashed line) given by Eqs.(1,2) with $\Theta_D = 280$ K, measured $C_e(T)$ and $C_l(T)$ - see inset to Fig. 2, and $g_\infty = 2.6 \times 10^{15}$ W/mol K. Similar to Au or Ag, we find good agreement at $T \gtrsim 200$ K, while below 40 K instead of showing a $\tau_{ep} \propto T^{-3}$ divergence, $\tau_r$ saturates.

In order to explain the discrepancy, we have carried out numerical simulations using coupled Boltzmann equations. Here, for example, the net phonon absorption by electrons with energy $\epsilon$ is represented by $\left[ \frac{d\epsilon_{ep}}{dt} \right]_{abs} = \int d\omega K_{ep}(\epsilon) D_p(\omega) D_e(\epsilon + \omega)$, where $D_e(\epsilon)$ and $D_p(\omega)$ are the electron and phonon DOS, and $S(\epsilon, \omega) = f_{\epsilon + \omega}(1 - f_\epsilon) - b_\omega(f_\epsilon - f_{\epsilon + \omega})$, with $f$ and $b$ being the electron and phonon distribution functions, respectively. $K_{ep}$ in the above equation and $K_{ee}$ in e-e scattering represent the square of the scattering matrix element, combined with all other numerical factors. When performing numerical simulations, a thermal phonon distribution ($b_{t=0} = b_0(T_l)$) and a non-thermal electron distribution ($f_{t=0} = f_0(T_e) \pm \delta f$) was taken as the initial condition just after the laser pulse, while $\tau_{ep}$ is found by fitting the total electron energy versus time curve to an exponential decay function. The initial perturbation $\delta f$ is around $10^{-5} \sim 10^{-3}$ for the energy range between $0.10 \sim 0.15$ eV above and below $E_F$, which is small enough that the increase in the temperature after e-ph thermalization is less than 1 K over the whole temperature range - consistent with the small excitation intensity used in the experiment. The phonon and electron DOS used in the simulation were chosen such that they fit the specific heat data (i.e. for the phonon DOS, we use the Debye model $D_p(\omega) \sim \omega^2$ with $\hbar \omega_D = 24$ meV, while $D_e(E_F) \approx 2.1$ eV$^{-1}$ f.u.$^{-1}$spin$^{-1}$). The result of the simulation using the absolute value of $K_{ep} = 0.93$ ps$^{-1}$eV and $K_{ee}/K_{ep} = 700$ is plotted by open circles in Fig.2. As expected, the simulation gives the same result as the TTM at high-T, while at low-T $\tau_{ep}$ saturates in
agreement with the experimental $\tau_r$.

Figure 3 shows $\tau_r(T)$ obtained on YbAgCu$_4$. At high temperatures ($T > T_K$) the value of $\tau_r$ is similar to LuAgCu$_4$. At low temperatures, however, $\tau_r$ increases by more than 2 orders of magnitude. Since heavy fermions are characterized by a peak in the DOS at $E_F$, the appropriate $D_{el}(\epsilon)$ should be used when modeling $\tau_{ep}(T)$. In our calculation we used $D_{e}(\epsilon) = D_{\text{peak}} \exp[-(\epsilon/\Delta)^2] + D_0$, where $D_{\text{peak}} = 70$ eV$^{-1}$f.u.$^{-1}$spin$^{-1}$, $\Delta = 13$ meV and $D_0 = 2.1$ eV$^{-1}$f.u.$^{-1}$spin$^{-1}$ (identical to the value for LuAgCu$_4$). It reproduces the experimental T-dependence of $C_e$, as shown in the inset to Fig.3. For simplicity we choose $E_F$ at the center of the peak, so that the chemical potential is constant. Since $D_{e}(E_F)$ is almost two orders of magnitude larger than in LuAgCu$_4$ we expect that the e-e thermalization is much faster in YbAgCu$_4$, and that the TTM would be valid at the lowest temperatures.

The calculated $\tau_{ep}(T)$ using Eq.(2) is plotted in Fig.3 by the dashed line. Here the approximate $C_e(T)$ and $C_l(T)$ were used, $g_\infty$ was taken to be the same as for LuAgCu$_4$, while $\chi(x,T)$ was evaluated explicitly for the above $D_{e}(\epsilon)$ and $F = 1$. Since $\tau_{ep}^{-1} \propto D_{e}$, and $D_{e}(E_F) \gg D_0$ the result is not surprising, implying that the simple TTM cannot account for the observed dramatic increase in $\tau_r$ at low temperatures. We should note that neither the value of the e-ph coupling constant $g_\infty$ nor $D_0$, which determine the absolute value of $\tau_{ep}$, are necessarily the same in YbXCu$_4$ and LuXCu$_4$. However, even if the e-ph coupling is 10 times smaller in YbAgCu$_4$ compared to LuAgCu$_4$ (which would give 10 times larger value of $\tau_{ep}$ - as plotted by dashed line in Figure 3), the observed T-dependence of $\tau_r$ still cannot be accounted for.

In order to account for the observed $\tau_r(T)$ we have to consider the nature of the electronic states within the peak in the DOS. In heavy fermions the peak in $D_{e}(\epsilon)$ originates from hybridization of the localized $f$-levels with the conduction band electrons. We hypothesize that the e-ph scattering within the DOS peak is suppressed, since the band dispersion near $E_F$ is much weaker than in regular metals. Therefore it is quite possible that the Fermi velocity $v_F$ is smaller than the sound velocity $v_s$, in which case momentum and energy conservation prohibit e-ph scattering when both initial and final electron states lie within the energy range where $v_F < v_s$. Assuming a parabolic band with $E_F \sim T_K \sim 100$ K, and 0.85 carriers per formula unit, one obtains $v_F \sim 4$ km/sec, while the longitudinal sound velocity for YbIn$_{1-x}$Ag$_x$Cu$_4$ ($x < 0.3$) is $\approx 4.4$ km/sec along [111] direction (similar $v_s$ is expected for YbAgCu$_4$). Even though a parabolic dispersion relation is just a rough
approximation, and a direct measurement such as de Haas-van Alphen effect is required to obtain $v_F$, our simple estimate supports this idea.

Using this hypothesis, good agreement with the data can be obtained. $\tau_{ep}(T)$ obtained by numerical simulations based on Boltzmann equations with $K_{ep}$ set to 0 for processes where the initial and final electronic state are in the range of $-24 < \epsilon < 24$ meV (i.e. within the DOS peak), and $K_{ep} = 0.23$ ps$^{-1}$eV otherwise, is plotted by open circles in Fig. 3. Even better agreement with the data is obtained from the TTM, assuming that the e-ph interaction strength $F(\epsilon, \epsilon')$ entering Eq.(3) smoothly vanishes as $\epsilon$ and $\epsilon' \rightarrow E_f$, accounting for $v_F$ variation (and thus $v_F < v_s$ condition) across the Fermi surface. This is implemented into the TTM simulation by approximating the factor $D_{ie}(\epsilon) D_{ie}(\epsilon') F(\epsilon, \epsilon')$ in Eq.(3) with the symmetrized function $(D_{ie}(\epsilon) D_{ie}(\epsilon') + D_{ie}(\epsilon') D_{ie}(\epsilon) - D_{ie}(\epsilon) D_{ie}(\epsilon'))$, where $D_{ie}(\epsilon) = D_0 - D_0 \exp[-(\epsilon/\Delta')^2]$. The resulting $\tau_{ep}(T)$, using $\Delta' = 24$ meV, and $g_\infty = 4.5 \times 10^{14}$ W/mol K is plotted by the solid line in Fig. 3. Indeed, extremely good agreement with the data is obtained, even though $\tau_r$ spans more than two orders of magnitude.

With the hypothesis that e-ph scattering is suppressed in the DOS peak, the experimental observation of anomalous T-dependence of $\tau_r$ can be understood. Namely, at $T < T_K$ the $C_e(T)$ increases dramatically compared to normal metals. On the other hand e-ph relaxation becomes more and more difficult as temperature is lowered since most of the electron relaxation should occur within the DOS peak, where the e-ph scattering is blocked by energy and momentum conservation. Therefore, the thermalization between electrons and the lattice occurs very slowly, giving rise to the divergent $\tau_{ep}$ below $T_K$. While the presented model explains the main features of the data, i.e. the low-T divergence of $\tau_{ep}$, there are still several issues requiring further experimental and theoretical effort.

For example, in the simulations we considered a temperature independent peak in the DOS, assuming that many-body and correlation effects can be described by effective, T-independent model parameters. This may be an oversimplification of the physics of heavy-fermion systems. However, the relaxation time simulations and specific heat calculations of our phenomenological model depend only weakly on a T-dependent DOS, as long as the peak width in the DOS does not vary faster than temperature. Further, it would be interesting to investigate e-ph thermalization in Kondo insulators. Namely, due to the presence of the gap near $E_F$ one would expect effects similar to the Rothwarf-Taylor bottleneck observed in superconductors. Secondly, even more interesting effects are expected due to the strong
reduction of the screening at low frequencies (below the gap) which could lead to non-adiabatic phonons.

In conclusion, we have utilized ultrafast optical spectroscopy to study the dynamics of photoexcited quasiparticles in HF compounds. We have observed a divergence in the e-ph thermalization time at low temperatures. We argue that the dramatic hundred-fold increase in the relaxation time at low temperatures in YbXCu$_4$ (and the lack of this quasi-divergence in the non-HF LuXCu$_4$ analogs) results from the largely increased DOS at $E_f$ coupled with strongly suppressed scattering of heavy-electrons by phonons.

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**Figure Captions**

**Figure 1**

Normalized photoinduced reflectivity data (solid symbols) on (a) LuAgCu$_4$ and (b) YbAgCu$_4$ at various temperatures, together with best fits (see text) to the data - solid lines. The data have been vertically shifted for clarity.

**Figure 2**

a) Temperature dependence of relaxation time $\tau_r$ on LuAgCu$_4$ (solid circles), together with the TTM prediction (dashed line) and the result of the numerical simulation (open circles) including the non-thermal electron distribution. Inset: $C_e$ (dashed) and $C_l$ (solid line) of LuAgCu$_4$.

**Figure 3**

$T$-dependence of $\tau_r$ on YbAgCu$_4$ (solid circles), together with the corresponding $\tau_{ep}$ (multiplied by 10 for the presentation purpose) from simple TTM prediction (dashed line). Assuming suppressed scattering of heavy electrons by phonons due to $v_F < v_s$ condition, very good agreement with the data is obtained: open circles present the result of numerical simulation, while solid line presents the TTM simulation - see text. Inset: experimentally determined $C_e(T)$ for YbAgCu$_4$ (open circles), together with calculated $C_e(T)$ based on the model $D_e(\epsilon)$ - solid line. $C_e(T)$ of LuAgCu$_4$ (dashed line) is added for comparison.
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matrix element.
Figure 1

(a) Time [ps] vs. \( \Delta R/R \) for different temperatures: 300 K, 12 K.

(b) Time [ps] vs. \( \Delta R/R \) for temperatures 12 K, 18 K, 32 K, 42 K, 140 K, 270 K.
Figure 2

![Graph showing the relationship between $T$ and $\tau_r$, $\tau_{sp}$ with $C_p$ as an inset.](image-url)
Figure 3

\[ \tau, \tau_{ep} \text{ [ps]} \]

\[ C_p \text{ [J/mol K]} \]

\[ T \text{ [K]} \]