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Hybridization and superconducting gaps in heavy-fermion superconductor $PuCoGa_5$ probed via the dynamics of photoinduced quasiparticles

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Abstract

We have examined the relaxation of photoinduced quasiparticles in the heavy-fermion superconductor $PuCoGa_5$. The deduced electron-phonon coupling constant is incompatible with the measured superconducting transition temperature T_c, which speaks against phonon-mediated superconducting pairing. Upon lowering the temperature, we observe an order-of-magnitude increase of the quasiparticle relaxation time in agreement with the phonon bottleneck scenario - evidence for the presence of a hybridization gap in the electronic density of states. The modification of photoinduced reflectance in the superconducting state is consistent with the heavy character of the quasiparticles that participate in Cooper pairing.

The discovery of relatively high-temperature superconductivity in the Pu-based compounds $PuCoGa_5$ (T_c=18.5 K) and $PuRhGa_5$ (T_c=8.7 K) has renewed the interest in actinide materials research[1,2]. The Pu-based superconductors share the $HoCoGa_5$-type tetragonal lattice stucture with the Ce-based series of compounds ($CeRhIn_5$, $CeCoIn_5$, and $CeIrIn_5$) commonly referred to as "115" materials. In the Ce-based 115 compounds, $CeIrIn_5$ (T_c=0.4 K) and $CeCoIn_5$ (T_c=2.3 K), display superconductivity at ambient pressure[3–5]. Both Ce- and Pu-based 115 compounds display the heavy fermion behaviour resulting from the influence of $4f$ (Ce) and $5f$ (Pu) electrons. The most intriguing question concerns the origin of superconductivity (SC) in the 115 materials. In the Ce series, the d-wave symmetry of the SC order parameter and the proximity of SC order to magnetism have lead to a widespread belief that the unconventional SC is induced by antiferromagnetic spin fluctuations[5]. In the Pu compounds, two possible scenarios regarding the SC mechanism have been considered: one approach favors a magnetically mediated unconventional SC similar to that in $CeCoIn_5$. In the other scenario, the conventional SC is mediated by phonons[6,7], where the strength of the electron-phonon (*e-ph*) coupling λ is the crucial parameter that sets the superconducting transition temperature T_c.

In this Letter, we present a measurement of the *e-ph* coupling constant λ via the pump-probe optical study of the room-temperature relaxation time of photoinduced reflectance. We find that *e-ph* coupling ($\lambda = 0.2 - 0.26$) is too weak to explain the high T_c of $PuCoGa_5$ and that phonon-mediated superconductivity is unlikely in this material. Upon lowering the temperature in the normal state ($T > T_c$), we find an order-of-magnitude increase in the relaxation time consistent with a phonon bottleneck, similar to other heavy-fermion materials[8], which provides the first optical evidence of the presence of a hybridization gap in the electronic density of states (DOS). Below T_c, the photoinduced response exhibits dramatic changes that we ascribe to the opening of the superconducting (SC) gap at the Fermi level. The observed dynamics confirms that the same quasiparticles detected in the normal state, i.e., the heavy quasiparticles, also participate in the SC pairing. Our study is the first to directly probe the electronic structure of $PuCoGa_5$ in the SC state and corroborate that fact. Our results are consistent with the theoretical investigations[9,10], which find that the electronic structure is dominated by cylindrical sheets of Fermi surfaces with large $5f$ electron character, suggesting that the delocalized $5f$ electrons of Pu play a key role in the superconducting pairing.

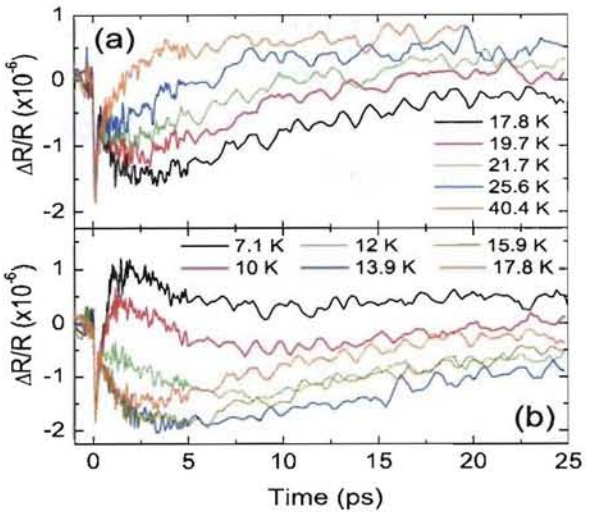

FIG. 1: (Color online) Phoroinduced reflectance of $PuCoGa_5$ at various temperatures.

In our experiment, 45-femtosecond optical pulses are used to photoexcite (pump) the material. The material's response is monitored using a weaker optical pulse (probe) that allows the measurement of pump-induced changes in the material's reflectance (photoinduced reflectance). By varying the time delay between the pump and probe pulses, we can record the evolution of the photoinduced reflectance with time resolution $\leq$ 100 fs (Fig. 1). Our pump-probe study was conducted on a clean as-grown surface of $PuCoGa_5$ single crystal grown in Ga flux[1]. We used an 80-MHz repetition rate Ti:sapphire laser producing 800-nm (1.55 eV) light pulses that were split into pump and probe parts. The probe pulses were focused onto a 30-μm spot, while the size of the pump spot was 60 μm. We used average pump powers of 0.5 mW and 1 mW, corresponding to pump fluences of 0.015 and 0.03 $\mu J/cm^2$. The probe average power was at least ten times lower. The small spot sizes and the high repetition rate provide the resolution of at least 1 part in 10^6 while minimizing sample heating by the pump.

In a metal, the pump pulse impinging on its surface creates an initial non-thermal distribution of electrons due to electronic absorption of photons[11,12]. The subsequent relaxation of this excited system is governed by electron-electron (*e-e*) and electron-phonon (*e-ph*) collisions. At high temperatures ($T \geq \theta_D/5$) in conventional metals[11], the *e-e* collisions happen at a much faster rate than the *e-ph* collisions. The non-thermal electronic distribution thermalizes through the *e-e* collisions before any exchange of energy between the electrons and

the lattice can take place, which leads to the difference in the effective electronic and lattice temperatures, T_E and T_L, respectively. After the electronic thermalization, the much slower equilibration of T_E and T_L proceeds with a characteristic time scale set by the strength of the *e-ph* coupling. This picture of quasiparticle dynamics holds in $PuCoGa_5$ at high temperatures $T \geq \theta_D = 240$ K[1] and the relaxation time of the photoinduced reflectance corresponds to the *e-ph* relaxation time τ_{EL}. Allen[13] showed that τ_{EL} is related to the *e-ph* coupling constant λ as

$$\tau_{EL} = \pi k_B T_E / 3\hbar\lambda \left\langle \omega^2 \right\rangle, \tag{1}$$

where $\langle\omega^2\rangle$ is the second moment of the phonon spectrum. We measured the room-temperature relaxation time in $PuCoGa_5$ to be $\tau_{EL}^{Pu} = 0.64 \pm 0.01$ ps (Fig. 2(c)).

The coupling constant λ is calculated using Eq. (1) and $T_E = 300$ K, since the initial pump-induced rise in electronic temperature $\Delta T_E(0) = T_E(0) - T_L(0) \ll T_L$. In the absence of the detailed knowledge about which phonon mode might be "responsible" for superconducivity in this material, we assume $\langle\omega\rangle^2 \leq \langle\omega^2\rangle \leq \theta_D^2$, where $\langle\omega\rangle = 212$ K was calculated by Piekarz *et al.*[14], and determine $0.2 \leq \lambda \leq 0.26$. Our estimate of λ represents the first experimental determination of the *e-ph* coupling in this material and can be compared to $\lambda = 0.7$ found in the *ab initio* calculation of Piekarz *et al.* By assuming a strong coupling limit[15] and using the simplified Allen-Dynes[16] formula for the SC transition temperature

$$T_c \approx \theta_D \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right] \tag{2}$$

with $\lambda = 0.26$ and $\mu^* = 0.1$ as a representative value of the effective Coulomb repulsion, we find $T_c \approx 0.027$ K (≈ 1.55 K in the upper limit of $\mu^* = 0$). This estimate of T_c disagrees with the measured transition temperature $T_c = 18.5$ K and reinforces the conclusion from similar estimates by Piekarz *et al.* and Bang *et al.*[6] (who used $\lambda = 1$) that the phonon origin of SC pairing in $PuCoGa_5$ is highly unlikely.

In conventional SCs, the room-temperature pump-probe measurements of λ were in excellent agreement with λ deduced from their SC transition temperatures[17]. Several pump-probe studies of cuprate superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ measured the *e-ph* relaxation time and found that the corresponding λ cannot account for the high T_c of that material ($\lambda < 0.25$ was found by Perfetti *et al.*[18] and $\lambda < 0.17$ was found by Zhu *et al.*[19]). The experimentally determined λ in $Bi_2Sr_2CaCu_2O_{8+\delta}$ compares favorably with the theoretical value calculated[20] for $YBa_2Cu_3O_7$ ($\lambda = 0.27$), which is expected to exhibit similar strength of the *e-ph* coupling.

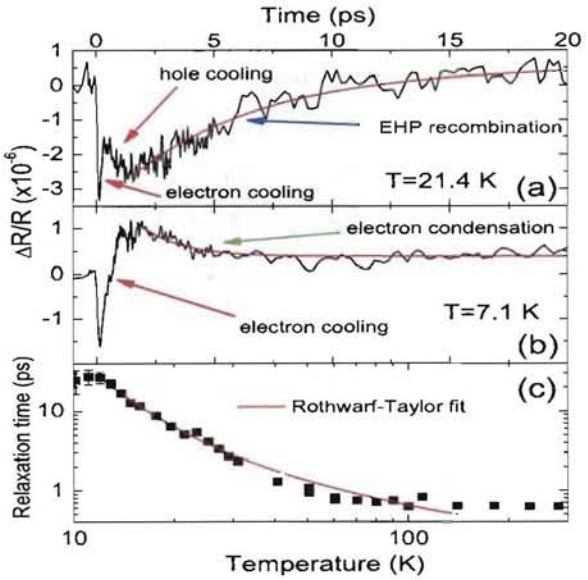

FIG. 2: (Color online) (a) Photoinduced reflectance in the normal state at $T > T_c$. (b) Photoinduced reflectance at $T < T_c$. The reflectance is modulated primarily by the change in the electron occupancy of states right above the hybridization gap. Red lines indiced the exponential fits of electron relaxation across the hybridization gap in the normal state and of electron condensation into the superconducting state below T_c. (c) Relaxation time of transient reflectance as a function of temperature in $PuCoGa_5$.

Upon lowering the temperature, the relaxation time in $PuCoGa_5$ increases by an order of magnitude between 100 K and 20 K (Figs. 1(a) and 2(c)). Similar increase of the relaxation time has been found in other heavy-fermion metals[8,21–23] and was ascribed to the hybridization gap in the electronic DOS. The hybridization gap results from the hybridization between the conduction band and the localized Pu f-electron states[8]. Since the magnitude of the gap is much smaller than energy of pump photons, the pump excites electrons into the states far above the hybridization gap (and holes into the states far below the gap). The subsequent relaxation of the photoexcited electrons proceeds via e-e collisions that lead to a quasiparticle multiplication effect[8,24]: each photon creates E_{photon}/Δ_{HG} (E_{photon} is the photon energy and Δ_{HG} is the magnitude of the hybridization gap) electron-hole (e-h) pairs that collect in the states just above and just below the gap. The subsequent decay of the e-h pair population is responsible for long relaxation of the photoinduced reflectance (blue arrows in

Figs. 2(a) and 3(a)).

The time evolution of the *e-h* pair density and the density of high-frequency phonons has been modeled using a system of coupled kinetic equations, known as the Rothwarf-Taylor (RT) model[25,26] and originally used to describe quasiparticle relaxation in SCs. The high-frequency phonons are intimately involved in the decay of *e-h* pairs, as a phonon with energy $\omega_{ph} \geq \Delta_{HG}$ is created upon *e-h* recombination. Since these phonons can subsequently excite *e-h* pairs, the decay of the *e-h* pair population is governed by the decay of the phonons. This process is often referred to as a phonon bottleneck. The RT model provides a means to calculate the temperature dependence of the relaxation time of photoinduced reflectance, which is governed by the thermally excited density of *e-h* pairs and high-frequency phonons, the bare rate of *e-h* pair recombination and creation, and the anharmonic decay time of the high-frequency phonons. The solution of the RT model is[26]

$$\tau(T) = \tau_0 \left\{ \delta[\epsilon n_T + 1]^{-1} + 2n_T \right\}^{-1}, \tag{3}$$

where $n_T = \sqrt{T}\exp(-\Delta_{HG}/2T)$ is the population of the thermally excited quasiparticles, and τ_0, δ, ϵ, and Δ_{HG} are temperature independent fitting parameters. Figure 2(c) shows the RT fit of the temperature dependence of the *e-h* recombination time τ where the magnitude of the hybridization gap is found to be $\Delta_{HG} = 88 \pm 14$ K ($\approx 61\,\mathrm{cm}^{-1}$). Since the relaxation time is determined by the indirect gap, the hybridization gap values deduced from these pump-probe measurements in other heavy-fermion metals tend to be smaller than those found in optical conductivity studies[8,22,23] which probe the direct gap. The characteristic temperature dependence of the relaxation time of Fig. 2(c) is a signature of a gap in the electronic DOS, thus providing the first spectroscopic evidence of the hybridization gap in $PuCoGa_5$.

At temperatures $16 < T < 25$ K, two initial processes can be distinguished before the *e-h* recombination takes place (Fig. 2(a)). The first process is very fast with characteristic time of $\tau_e \leq 200$ fs and leads to a partial recovery of the initial drop in reflectance. The second is a slower process with characteristic time of $\tau_h \leq 1$ ps, which further lowers the reflectance until the *e-h* recombination starts (at the delay of 2-3 ps in Fig. 2(a)) . The long (up to 10 ps) rise-time dynamics was observed below 25 K in several other heavy-fermion metals[8] and the superconductor MgB_2[27]. In those studies, the long rise time was attributed to the competition between the *e-ph* and *e-e* scattering channels at low temperatures that

leads to excess high-frequency phonon population and slows down the e-h multiplication. We suggest that in our measurements, the two initial processes correspond to electron (τ_e) and hole (τ_h) cooling that take place after the e-h multiplication. The assignment of the slower τ_h process as the hole response follows from its weakening and eventual disappearance below T_c, as we show below.

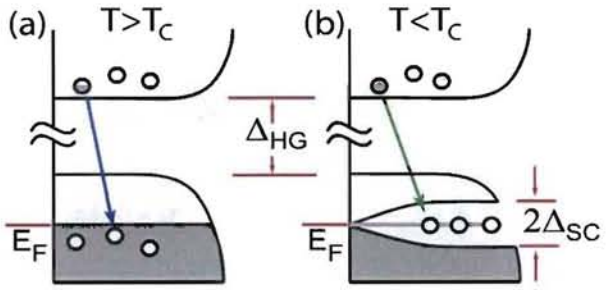

FIG. 3: (Color online) A diagram of electronic structure consistent with our experiments. (a) Electron-hole pair recombination across the hybridization gap above T_c. Rothwarf-Taylor bottleneck occurs. (b) Electron relaxation across the hybridization gap and into the superconducting condensate below T_c.

In conventional metals, the characteristic time of e-e collisions[8,12] is $\leq$ 100 fs - within this time electrons form a thermal distribution with an elevated temperature $T_E > T_L$. In heavy fermion metals, e-e collisions set the time scale of 100 fs for e-h multiplication, after which the electron and hole cooling and e-h recombination govern the dynamics (Figs. 2(a) and 3(a)) and the change in reflectance results from the change in the occupancy of the electronic states just above the hybridization gap and hole states just below the gap. (We now make explicit the assumption made in the previous paragraph and in Fig. 3, i.e., that the Fermi level lies below the hybridization in our picture of a single conduction band hybridized with a single Pu $5f$ band[28]. Our choice of the Fermi level does not diminish the generality of our conslusions, as placing the Fermi level above the hybridization gap allows the construction of an equally valid description where electrons and holes are interchanged.)

In the following, we reasonably assume that the e-h multiplication stops after $\leq$ 100 fs, the characteristic time of e-e collisions and electronic thermalization[8,12]. We also assume that the change in reflectance results from the change in the occupancy of the electronic states just above the hybridization gap and hole states just below the gap. After the e-h

multiplication stops, electron and hole cooling and e-h recombination govern the dynamics[28] (Figs. 2(a) and 3(a)). The cooling starts when the average energy of an e-h pair becomes lower than $2\Delta_{HG}$ and proceeds via the e-ph collisions that lower the effective temperatures of electrons and holes. Below 25 K, the electron and hole cooling are clearly resolved in the time domain (red arrows in Fig. 2(a)). The electron cooling is accompanied by the recovery of reflectance, i.e., the increase in the electron occupancy at hybridization gap edge increases the reflectance. By contrast, the hole cooling is accompanied by a further drop in reflectance, which means that the hole occupancy at the gap edge reduces reflectance. The differing cooling times can result from electrons and holes occupying different regions of the Brillouin zone, which leads to differing strengths of their coupling to phonons. These considerations allow us to understand the changes in the photoinduced reflectance spectra that happen below the superconducting transition temperature $T_c \approx 17$ K.

Below T_c, the drop of the photoinduced reflectance due to hole cooling begins to diminish (Fig. 1(b)), indicating the reduced modulation of the hole occupancy at the lower hybridization gap edge caused by the optical pump. We attribute this reduction to the development of the SC gap at the Fermi level, which we assume to lie just below the gap (Fig. 3). In photoexcited SCs, quasiparticle multiplication occurs at the expense of the superconducting condensate[12,24]. Similarly, quasiparticle multiplication in $PuCoGa_5$ below T_c happens via the destruction of the SC condensate. Electrons are created in this process, but the hole density is not modified, thus leading to the disappearance of the hole-occupancy signature from the photoinduced reflectance at the lowest temperatures (Fig. 2(b)). The remaining photoinduced response evolves from the electronic-cooling component: the fast initial recovery seen above T_c gets stronger and eventually evolves into a feature that peaks at about 1-2 ps and then decays on the time scale of ≈ 2 ps (Fig. 2(b)). This response at the lowest temperature is due solely to the photoinduced evolution of the electron occupancy above the hybridization gap. The 2-ps decay results from the electronic relaxation across the hybridization gap and condensation into the superconducting state (green arrows in Figs. 2(b) and 3(b)). The behavior of the photoinduced reflectance below T_c suggests that the quasiparticles that form the SC condensate are the same heavy quasiparticles formed by the opening of the hybridization gap. This conclusion agrees with the measurements of the specific heat and the critical field H_{c2} that indicate the enhanced effective mass of the condensing quasiparticles[1,29]. Our observations provide the spectroscopic evidence for

superconductivity in $PuCoGa_5$ developing on the heavy quasiparticle band.

In conclusion, we measured the *e-ph* coupling constant in $PuCoGa_5$ to be $\lambda = 0.2 - 0.26$, which rules out phonon-mediated SC pairing. We present the first direct spectroscopic evidence for hybridization gap in the electronic DOS in the normal state and for the formation of the SC condensate from heavy quasiparticles arising from hybridization of the Pu $5f$ electrons and the conduction electrons, both of which indicate magnetically mediated superconductivity in this material. This is consistent with a growing body of evidence[15,29,30] that suggests a d-wave order parameter in the transuranic superconductors ($NpPd_5Al_2$, $PuCoGa_5$, $PuRhGa_5$), similar to most of the other known heavy fermion superconductors.

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[28] Our analysis is based on the single-band electronic structure at the Fermi level. In a more realistic picture, electrons and holes could belong to different sheets of the Fermi surface and quasiparticle multiplication and cooling could be happening across multiple bands. The assignemt of observed relaxation as electron and hole processes is not unique: equally valid is the picture where electrons and holes are interchanged. These considerations do not affect our conclusions, as the longest observed relaxation is undoubtedly due to electron-hole recombination across a gap in the density of states.

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