Hybridization gap versus hidden order gap in URu$_2$Si$_2$ as revealed by optical spectroscopy

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We present the in-plane optical reflectance measurement on single crystals of URu$_2$Si$_2$. The study revealed a strong temperature-dependent spectral evolution. Above 50 K, the low frequency optical conductivity is rather flat without a clear Drude-like response, indicating a very short transport life time of the free carriers. Well below the coherence temperature, there appears an abrupt spectral weight suppression below 400 cm$^{-1}$, yielding evidence for the formation of a hybridization energy gap arising from the mixing of the conduction electron and narrow f-electron bands. A small part of the suppressed spectral weight was transferred to the low frequency side, leading to a narrow Drude component, while the majority of the suppressed spectral weight was transferred to the high frequency side centered near 4000 cm$^{-1}$. Below the hidden order temperature, another very prominent energy gap structure was observed, which leads to the removal of a large part of the Drude component and a sharp reduction of the carrier scattering rate. The study revealed that the hybridization gap and the hidden order gap are distinctly different: they occur at different energy scales and exhibit completely different spectral characteristics.

PACS numbers: 74.25.Gz, 74.70.Xa, 75.30.Fv

URu$_2$Si$_2$ has attracted considerable interest in the last two decades due to its intriguing physical properties and multiple phase transitions. URu$_2$Si$_2$ shows behavior typical of heavy fermion metals: its resistivity increases slightly with decreasing temperature, reaches a maximum at about 70 K, then decreases fast below 40-50 K. The behavior is consistent with the expectation for the crossover of U 5f electrons from localized behavior with the formation of local magnetic moments to itinerant transport in Kondo lattice. In this picture the conduction electrons change from a state of experiencing strong scattering from local moments of U 5f electrons to a heavy Fermi liquid state by screening the moment through a singlet coupling at low temperature. At $T_{HO}$ = 17.5 K, the compound shows a prominent second order phase transition characterized by a large jump in heat capacity. Despite many years of study and countless theoretical proposals, the order parameter remains unknown. It is therefore referred to as "hidden order" (HO) state. A tiny magnetic moment formation (0.03 $\mu_B$/U) was determined, but it is too small to explain the large entropy loss seen in the specific heat. Suggestions for the mysterious order include charge and/or spin density wave formation (CDW/SDW) from itinerant U 5f electrons or multipolar or orbital orderings in terms of localized 5f electrons, but no consensus has yet been reached. Of further interest, a superconducting transition occurs at much lower temperature $T_c$ = 1.5 K.

A number of experiments indicate that the HO phase transition is accompanied by the formation of partial energy gap or reconstruction of the Fermi surface. However, some other recent spectroscopic measurements revealed that the energy gap does not close at the HO transition temperature $T_{HO}$, but persist to a higher temperature near 25-30 K. A hidden order pseudogap state has been suggested and examined both experimentally and theoretically. In principle, the HO energy gap could be obscured by the formation of a hybridization gap, a typical feature of heavy fermion metals. This energy gap arises from the hybridization of conduction electrons with the flat band of heavy f-electrons in the Kondo lattice Fermi liquid state. The controversial information about energy gaps yielded by different experiments could be a result of mixing of multiple energy gaps. It is essential to have a clear picture about the energy gaps in order to understand the complex behavior of URu$_2$Si$_2$. In particular, one should clarify how the hidden order energy gap is related to the hybridization gap, and whether a HO pseudogap is actually present?

Optical spectroscopy is a powerful technique to investigate charge dynamics and band structure of materials as it probes both free carriers and interband excitations. In particular, it yields direct information about formation of energy gaps. Infrared spectroscopy studies on URu$_2$Si$_2$ were reported by several groups previously. Early measurements clearly revealed a partial energy gap formation below the HO phase transition, but those studies did not address possible hybridization energy gaps. On the other hand, a recent infrared study indicated that there is a pseudogap formation below 30 K in URu$_2$Si$_2$. The feature was suggested to be a precursor of the HO phase transition at 17.5 K. In this work, we present a systematic study of single crystals of URu$_2$Si$_2$. We show that both the hybridization gap and the HO gap are present in the spectral data, but they occur at different energy scales and exhibit completely different spectral characteristics. Our measurement indicates that the peculiar
spectral feature just above the HO temperature is related to the hybridization energy gap and cannot be taken as a precursor of HO phase transition. No pseudogap specific to the HO phase transition is detected.

Single crystals of URu$_2$Si$_2$ were grown by the Czochralski method, using a continuous gettered tri-arc furnace under Ar gas starting from stoichiometric amounts of the constituent materials. No additional heat treatment was performed. The in-plane dc resistivity from 2 to 300 K, measured by a standard four-probe method in a Quantum Design Physical Properties measurement system (PPMS) is shown in Figure 1. In agreement with previous work, the resistivity increases slightly with decreasing temperature from 300 to 70 K, then decreases somewhat with further decreasing temperature. A much faster decrease could be seen below 40~50 K. The sharp anomaly at 17.5 K shown in the expanded region in the inset is attributed to the HO phase transition.

We performed optical measurements on a cleaved in-plane surfaces of URu$_2$Si$_2$ using Bruker 113v, Vertex 80v and a grating-type spectrometers in the frequency range from 17 to 50000 cm$^{-1}$. An in situ gold and aluminium overcoating technique was used to get the reflectance $R(\omega)$. We obtained the real part of conductivity $\sigma_1(\omega)$ by the Kramers-Kronig transformation of $R(\omega)$. A Hagen-Rubens relation was used for low frequency extrapolation and a $\omega^{-1}$ dependence was used for high frequency extrapolation up to 300000 cm$^{-1}$, above which a $\omega^{-4}$ dependence was employed.

Figure 2 shows the reflectance spectra $R(\omega)$ of URu$_2$Si$_2$ for several different temperatures. The upper panel shows the $R(\omega)$ at room temperature up to 50000 cm$^{-1}$, the lower panel shows the temperature-dependent spectra in an expanded low frequency region within 500 cm$^{-1}$. Two step-like features could be clearly seen near 3500 cm$^{-1}$ (~0.44 eV) and 16000 cm$^{-1}$ (~2 eV) in $R(\omega)$ in the upper panel. They lead to two broad peaks in conductivity spectrum $\sigma_1(\omega)$ as displayed in the inset of Figure 3, which we attribute to interband transitions.

Very intriguing temperature-dependent spectra are seen at low frequencies as shown in the lower panel of Fig. 2. The reflectance values decrease slightly with decreasing temperature from 300 K to 50 K, indicating a non-metallic temperature-dependent response, which is consistent with the dc resistivity behavior. Much clearer differences in $R(\omega)$ are seen from 50 K to 20 K. The reflectance value above 130 cm$^{-1}$ is obviously lower than that at higher temperatures. However, $R(\omega)$ shows an upturn below about 130 cm$^{-1}$ so that the very low-frequency $R(\omega)$ values exceed those at higher temperatures. Below the HO phase transition, another pronounced spectral feature appears: The $R(\omega)$ spectrum is severely suppressed below 60 cm$^{-1}$, but increases steeply at ($\omega \leq 30$ cm$^{-1}$) lower frequencies, leading to a pronounced dip feature. This structure is clearly seen in $R(\omega)$ at 8 K and is still present at 15 K.

The evolution of the electronic states is more clearly reflected in the conductivity spectra. Figure 3 shows the $\sigma_1(\omega)$ spectra at different temperatures. The upper panel shows the $\sigma_1(\omega)$ up to 60000 cm$^{-1}$, the lower panel shows the spectra in the expanded low frequency region below 500 cm$^{-1}$. The inset shows $\sigma_1(\omega)$ up to 30000 cm$^{-1}$ at room temperature; the two interband transition peaks can be clearly seen. There are a number of important temperature-induced spectral features. First, for tem-
temperature higher than 50 K, the Drude component is virtually invisible. $\sigma_1(\omega)$ show little temperature dependence below 2000 cm$^{-1}$ at room temperature. A slight decreasing tendency with decreasing frequency is seen at lower temperature. As is well known, the width of Drude peak is linked with the scattering rate (or inverse of the transport lifetime) of the quasiparticle; the measurement result indicates that there are no well-defined quasiparticles with sufficiently long transport lifetimes above 50 K, indicating that the conduction electrons experience extremely strong scatterings from the local U 5f moments. Consistent with the dc resistivity measurement, the low frequency conductivity is suppressed with decreasing the temperature from 300 K to 50 K. The suppressed spectral weight below 1500 cm$^{-1}$ is transferred to higher-$\omega$ region centered at about 3500 cm$^{-1}$.

Second, in the deeply coherent state, for example at 20 K, there appears an abrupt spectral weight suppression below 400 cm$^{-1}$ in conductivity spectrum, so that the spectral curve separates itself clearly from the spectra at temperatures above 50 K. Similar spectral shapes were observed in two recent works. A small part of the suppressed spectral weight was transferred to the low frequency side, leading to the formation of a narrow Drude component, while the majority of the suppressed spectral weight is still transferred to the high-$\omega$ side centered near 3500 cm$^{-1}$. The sharp suppression of $\sigma_1(\omega)$ below 400 cm$^{-1}$ is an indication of the development of an energy gap. The energy level at which the conductivity reaches the lowest value could be taken as the gap amplitude, which is about 130 cm$^{-1}$ (~16 meV). This energy gap is associated with the development of the coherent metallic state due to the mixing of conduction electron band with the flat 5f electron band, it is therefore the hybridization energy gap. The narrow Drude component is derived from the heavy quasiparticles. The rapid increasing feature is already beyond the low frequency limit in our measurement and in the extrapolation region. Nevertheless, the extrapolated curve is verified from a reasonably good match between the extrapolated zero-frequency limit and the dc conductivity value. The small spectral weight of the Drude component is attributed to the heavy quasiparticle effective mass.

The pronounced peak near 3500 cm$^{-1}$ should originate predominantly from the interband transitions shown in the inset of Fig. 3. However, the temperature-induced spectral weight transfer from low frequency to this energy level must have a different origin. One possibility is that the spectral enhancement at such high energy comes from the incoherent part of the quasi-particle spectral function driven by the on-site Coulomb repulsion energy (Hubbard U). The presence of incoherent structures at intermediate frequencies of the order U/2 to U is supported by dynamical mean-field theory calculations. Nevertheless, the energy scale to which the spectral weight is transferred depends on the individual compound. For another prototype HF compound, CeCoIn$_5$, the suppressed spectral weight is transferred to only around 700 cm$^{-1}$ much lower than the energy scale we infer for URu$_2$Si$_2$.

The third important feature is the observation of the prominent energy gap structure below the hidden order transition temperature $T_{HO}$ which leads to the removal of a large part of the Drude component. Consistent with previous optical measurements, a further narrowed Drude component is left in the extrapolation region. Since the width of the Drude component is the quasiparticle scattering rate, the opening of the partial energy gap also leads to a sharp reduction of the carrier scattering rate. It is worth noting that the removed spectral weight is piled up just above the energy gap, resulting in a sharp coherent spectral peak at about 65 cm$^{-1}$ (~8 meV), as seen in earlier reports. This spectral feature is very different from the formation of the hybridization energy gap which induces a spectral weight transfer to much higher energy levels. This indicates that the HO energy gap is completely different from the hybridization energy gap. It is also worth noting that the formation of hybridization gap is a crossover phenomenon and not associated with a thermodynamic phase transition such as in the case of the HO gap.

The above mentioned spectral weight transfer can
be seen more clearly in the normalized spectral weight plot shown in Fig. 4. The spectral weight is defined as \( SW = \int_0^\infty \sigma_1(\omega)d\omega \), where \( \omega_c \) is a cut-off frequency. For clarity we present only the low-temperature normalized spectra \( SW(T)/SW(70 \text{ K}) \). In the figure, the low-frequency part of \( SW(20 \text{ K})/SW(70 \text{ K}) \) is much higher than unity, suggesting the development of Drude component at low temperature. However, the normalized spectral weight becomes smaller than unity above 120 cm\(^{-1}\) due to the formation of the hybridization gap. It reaches a minimum, then increases slowly again. The spectral weight is almost fully recovered near 5000 cm\(^{-1}\). Obviously, the spectral weight transfer related to the hybridization gap formation occurs over a broad energy scale. In the \( SW(8 \text{ K})/SW(70 \text{ K}) \) plot, the spectrum becomes less than unity below 30 cm\(^{-1}\), reaching a minimum near 50 cm\(^{-1}\), then increasing sharply to almost unity near 80 cm\(^{-1}\). This is due to the HO energy gap formation. The second dip at a higher energy scale and the gradual recovery up to 5000 cm\(^{-1}\) could again be attributed to the spectral weight redistribution associated with the hybridization energy gap.

The nature of HO remains unknown at present; nevertheless, the shape of the energy gap provides some hint to this issue. The pronounced peak in \( \sigma_1(\omega) \) is a characteristic structure of the "density wave"-type energy gap excitation.\(^{31,32}\) It arises from the "case I" coherent factor effect in the mean-field BCS-like condensate. In the BCS formalism, the "case I" coherent factor is for density wave (either charge density wave or spin density wave) condensate arising from the nesting-induced FS reconstruction, and "case II" coherent factor is for superconducting condensate.\(^{31,32}\) For the latter case, the \( \sigma_1(\omega) \) only shows a smooth onset at the energy gap. For \( URu_2Si_2 \), the shape of the energy gap is almost a "text book"-like example of "case I" coherent factor, where the location of the pronounced peak in \( \sigma_1(\omega) \) could be identified as the energy gap, i.e. \( 2\Delta \approx 65 \text{ cm}^{-1} (8 \text{ meV}) \). We are not aware of any other gap-formation mechanism which could produce such a sharp peak structure in \( \sigma_1(\omega) \). We noticed that recent density-function theory studies have indicated the presence of two strongly nested FS sheets separated by a nesting vector \( Q_0 = (0,0,1) \) in the paramagnetic bct phase.\(^{9,33,34}\) The nesting wave vector is identical to the commensurate AF wave vector revealed by the inelastic neutron scattering experiments.\(^{5,8}\) So, we believe that the HO is at least related to some type of density wave associated with the nesting instability of the FS.

The energy scale of the HO energy gap detected here is in good agreement with the gap energy scale obtained by a number of other spectroscopic techniques, for example, scanning tunnelling microscopy (STM) measurement.\(^{20}\) The energy scale of the hybridization energy gap is also in good agreement with that obtained by recent point contact tunnelling spectroscopy experiment.\(^{22}\) However, the latter measurement failed to probe the energy gap associated with the HO phase transition at lower temperature.

Finally, we shall make rough estimates of the mass enhancement in the heavy fermion coherent state and the change of the Drude component in the HO state. In principle, the spectral weight of the Drude component, being equal to the square of the plasma frequency, could be calculated through the sum rule, \( \omega_p^2 = 8 \int_0^\infty \sigma_1(\omega)d\omega \). The integration up to X should cover all the spectrum contributed by the free carriers but still below the interband transition. Because the conductivity spectrum of \( URu_2Si_2 \) at high temperature is rather flat due to very strong scattering from the U 5f moments, it is difficult to separate the Drude component from the interband transition. Roughly we take X=1500 cm\(^{-1}\) where we expect that there is a balance between the Drude component tail and the onset part of the interband transition, then we get \( \omega_p \approx 1.67 \times 10^4 \text{ cm}^{-1} \) for T=300 K. The spectral weight of the Drude component in the low-temperature coherent state could be more accurately determined because it separates distinctly from the remaining part in the conductivity spectra. Taking X=135 cm\(^{-1}\) for T=20 K, we get \( \omega_p \approx 4.28 \times 10^3 \text{ cm}^{-1} \). The small plasma frequency in the coherent state is due to the renormalization of the quasiparticle effective mass arising from the mixing with the heavy band of U 5f electrons. The mass enhancement could be obtained from the square of the ratio of the two plasma frequencies, \( \mu^* / \mu_B = |\omega(300 \text{ K})/\omega(20 \text{ K})|^2 \approx 15 \). The Drude component is further narrowed due to the opening of the partial HO gap in the HO state. Taking X=42 cm\(^{-1}\) for T=8 K, we get \( \omega_p \approx 2.09 \times 10^3 \text{ cm}^{-1} \). The smaller value relative to that at 20 K is mainly due to the removal of the FS or the reduction of itinerant carrier density. Assuming the carrier effective mass does not change below 20 K, the square of the ratio of the two plasma frequencies, \( |\omega(8 \text{ K})/\omega(20 \text{ K})|^2 \approx 0.24 \), reflects the residual carrier density left in the HO state. This means that roughly three quarters of FS is removed by the gapping of the
FS. On the other hand, the Drude component becomes further narrowed. Therefore, the opening of the partial gap strongly reduces the scattering channel. From all above analysis, we infer that the HO phase transition is best understood from the density wave type transition driven by the Fermi surface instability.

Acknowledgments

We acknowledge useful discussions with John Mydosh and Yifeng Yang. This work is supported by the National Science Foundation of China, and the 973 project of the Ministry of Science and Technology of China. Research at McMaster is supported by NSERC and CIFAR.

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