Chapter 5

Optical Spectroscopy of Heavy Fermion Systems

The optical properties of the heavy fermion family CeMIn$_5$ ($M = \text{Co, Rh, Ir}$) have been determined in the photon energy range from 2 meV to 4.5 eV using the combination of near normal incidence reflectivity (2 meV - 0.8 eV) and ellipsometry (0.8 - 4.5 eV). In all compounds, signatures of the formation of a coherent state are found. However, as a result of the competition with antiferromagnetism, the energy region where the coherent state occurs is much lower in the compound that orders magnetically. Furthermore, the optical properties of the non-magnetic counterpart of one of the members have also been determined.

5.1 Introduction

Cerium based compounds are well known to exhibit strongly correlated electronic phenomena. Among them, the materials of the CeMIn$_5$ ($M = \text{Co, Rh, Ir}$) group have recently attracted considerable attention. The reason is their unusual properties, especially their unconventional superconductivity similar to the high $T_c$ superconductors [116, 120] and, presumably, proximity to a quantum critical point (with pressure [120, 121] and magnetic field [119] as tuning parameters). The analogy with the high $T_c$ superconductors even starts with their crystal structure which can be seen as layers of CeIn$_3$ separated by MIn$_2$ layers (see Fig. 5.1). This has also raised the question of the effect of low dimensionality in heavy fermion systems. These heavy fermion compounds exhibit an ample gamut of properties that reveal the subtle interplay between magnetism and superconductivity [122] as it can be seen in their phase diagram which is shown in Fig. 5.2. CeCoIn$_5$ is the heavy fermion compound with the highest superconducting transition temperature, $T_c$, at ambient pressure (2.3 K) [117, 122]. CeRhIn$_5$ does not superconduct at ambient pressure but is an antiferromagnet below $T_N = 3.8$ K.
Finally, CeIrIn$_5$ superconducts at a relatively low temperature (0.4 K) and does not order magnetically [116].

The physics of a single magnetic impurity in a non-magnetic metallic matrix is characterized by a single temperature $T_K$ (Kondo temperature). Below $T_K$, the local moment of the impurity is screened by the conduction electrons and the system can be described as a Fermi liquid. Moreover, all thermodynamic quantities scale with the reduced temperature $T/T_K$. An important question in the Kondo lattice (a lattice of magnetic centers) is whether the temperature below which the moments are locally screened ($T_K$) coincides with the temperature below which the Fermi liquid is formed ($T^*$) and how these are related to the Kondo temperature of the single impurity [123]. Experimentally, $T^*$ is usually associated with $T_{coh}$ which is the temperature where the resistivity shows a maximum. If intersite interactions are not taken into account, calculations in the dynamical mean-field theory [123, 124] indicate that there are two completely different energy scales. The first one, $T_K$, coincides with that of the single impurity case while the second one depends only on the ratio between the conduction and f-electron densities, ($n_c/n_f$). It turns out that when $n_c/n_f \sim 1$, $T^*$ is slightly enhanced over $T_K$ but rapidly decreases as the exhaustion regime is reached ($n_c \ll n_f$). If, on the other hand, intersite interactions are considered [126], the single impurity and the

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**Figure 5.1:** Crystal structure of CeMIn$_5$ (adapted from Ref. [18]).
5.1. INTRODUCTION

lattice are characterized by two different Kondo temperatures.

In contrast with this point of view, from the study of the effect of substitution of the Ce atom by La in CeMIn$_5$ \((M = \text{Co, Rh, Ir})\), Nakatsuji et al \cite{127, 128} have proposed that the single impurity energy scale "survives" when going to the lattice with \(T^*\) being the result of intersite correlations. At high temperatures, the Kondo lattice behaves as a set of non-interacting magnetic impurities \((\text{Kondo gas})\) which condense below \(T^*\) \((\text{Kondo liquid})\). However, they suggest, the condensation is not complete when the material is close to a quantum critical point, and at low temperatures the material can be described as a two component system. Since there is no evidence for a spatial phase separation, what occurs below \(T^*\) is a transfer of spectral weight from the high frequency part of the spectrum (corresponding to the localized Kondo moments) to the low frequency part (corresponding to the coherent state). In the present work we present optical measurements in the CeMIn$_5$ family. We experimentally see how antiferromagnetism \((\text{AF})\) competes with the formation of the coherent state. This competition manifests itself in lower values for the characteristic energies of CeRhIn$_5$ in comparison to the compounds that do not order magnetically. We will see that the loss of spectral weight associated with the formation of the coherent state occurs in the same energy range for all three members of the CeMIn$_5$ family. Furthermore, the energy where this recovery occurs is much larger than the region where the mass enhancement occurs which seems to be a common feature in Kondo systems.

**Figure 5.2:** Phase diagram of CeMIn$_5$ \((\text{adapted from Ref. \cite{122}})\).
5.2 Optical Properties of CeMIn$_5$ (M = Co, Rh, Ir)

5.2.1 Experiment and Results

High quality single crystals of CeMIn$_5$ (M = Co, Rh, Ir) were obtained from an In-rich flux [116, 117, 118]. After polishing, the optical properties of the ab-plane were determined at different temperatures by combining reflectivity at near normal incidence (11°) and ellipsometry. The reflectivity (Fig. 5.3) was determined from 30 to 6000 cm$^{-1}$ using a Fourier transform spectrometer. The temperature dependence was measured using a home-built cryostat with the intensities calibrated against a gold reference film evaporated in situ on the sample. In the Co and Ir compounds, the overall behaviour of the reflectivity is similar to a previous study of CeCoIn$_5$ [129]: a metallic behavior at high temperatures and a strong temperature dependence especially below 2000 cm$^{-1}$ and 50 K which signals the development of the coherent state. In the Rh compound the temperature dependence is weaker.

Ellipsometry of the ab-plane, on the other hand, was performed from 6000 to 36000 cm$^{-1}$ with an ellipsometric spectrometer at an angle of incidence of 80°. At the same set of temperatures as the reflectivity experiment, spectra were taken using a home-made ultra high vacuum cryostat. These spectra give the pseudo-dielectric function which have to be corrected for the c-axis response. For this purpose we also measured, at room temperature, the near normal reflectivity of the ab-plane*. As an example, we show the results for CeCoIn$_5$ in the gray circles of Fig. 5.3(a). The correction was of less than 1% and, therefore, we have taken the ellipsometric spectra as the dielectric function.

5.2.2 Optical Conductivity and Hybridization Gap

From the complete data set, the complex dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i(4\pi/\omega)\sigma_1(\omega)$, was calculated in the infrared (30-6000 cm$^{-1}$) using Kramers-Kronig relations (KK), following the procedure described in Chapter 2. In Fig. 5.4 we show $\sigma_1(\omega)$ in the entire frequency range. The temperature dependence of the optical conductivity of the Co and Ir compounds at low frequencies follows closely what has been previously seen in other heavy fermion systems. Above $T_{coh}$ the optical conductivity can be described by a single Drude peak while below it, a minimum appears signaling the appearance of a more narrow Drude peak. The origin of this behavior is the development of the so-called hybridization gap, $\Delta$, as

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*For this measurement, we started with the sample with gold evaporated in its surface. The dielectric function of this film was determined first via ellipsometry. Later, in near normal incidence configuration, the intensity of the gold was measured. Then the gold film was removed and the intensity of the sample was also measured. The ratio of this two quantities, corrected by the gold reflectivity (obtained from the ellipsometric measurement), gives the high frequency reflectivity.
Figure 5.3: Reflectivity of the different samples at several temperatures. Below 6000 cm\(^{-1}\): measured. Above 6000 cm\(^{-1}\): calculated from the dielectric function. The gray dots show the measured reflectivity of the ab-plane of CeCoIn\(_5\). Insets: Reflectivity below 2000 cm\(^{-1}\).
Figure 5.4: Real part of the optical conductivity in the entire frequency range at several temperatures. The lower panel also shows the obtained $\sigma_1(\omega)$ if the high frequency reflectivity of Ref. [129] is used in the KK analysis (gray dotted line). Insets: Measured frequency dependent mass (solid lines) and obtained from a fit to the experimental data (dotted lines).
5.2. OPTICAL PROPERTIES OF CEMIN5 (M = CO, RH, IR)

Figure 5.5: Schematic representation of the optical conductivity in heavy fermion metals (from Ref. [136]). Referring to Fig. 1.9, the intraband transitions in the lower band produce the narrow Drude mode while the interband transitions between the two resulting bands produce the bump seen at higher frequencies.

When comparing our results for CeCoIn5 with those of a previous report [129], we notice that both show the minimum in $\sigma_1(\omega)$ at the same position and a shoulder at 250 cm$^{-1}$. The later feature was interpreted as a Holstein band (an absorption corresponding to the bosons that couple the electrons in the SC state) inside of the gap which could be attributable to AF critical fluctuations [129, 127]. The argument for such assignment is that, in contrast with what has been seen in other heavy fermion systems [130], there is not a sudden decrease of the optical conductivity just below the peak originated by the transitions across a result of the hybridization between the conduction electrons and the localized f-moments [17] (for a schematic representation of this situation see Fig. 1.9). The intraband transitions in the lower band produce the narrow Drude mode while the interband transitions between the two resulting bands produce the bump seen at higher frequencies [17, 131, 132, 136] (see Fig. 5.5). In the Rh compound these characteristics are less strong but still a decrease in the optical conductivity can be seen at low frequencies. Since this compound eventually becomes AF at 3.8 K, this seems to be the result of the competition between the magnetic ordering and the coherent state. We will discuss more about this point below.
Table 5.1: Characteristics parameters of CeMIn$_5$. $T^*$ is taken from Refs. [127, 128]. $T_{coh}$ was calculated from the DC resistivities of Refs. [116, 117, 118] while $\gamma$ was taken from the same References. $m^*/m$ has been calculated from spectral weight considerations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\omega^*$ (cm$^{-1}$)</th>
<th>$\omega_1$ (cm$^{-1}$)</th>
<th>$T^*$ (cm$^{-1}$ (K))</th>
<th>$T_{coh}$ (cm$^{-1}$ (K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeCoIn$_5$</td>
<td>140</td>
<td>200</td>
<td>31 (45)</td>
<td>31 (45)</td>
</tr>
<tr>
<td>CeRhIn$_5$</td>
<td>$&lt;$100</td>
<td>$&lt;$100</td>
<td>10 (15)</td>
<td>28 (41)</td>
</tr>
<tr>
<td>CeIrIn$_5$</td>
<td>120</td>
<td>220</td>
<td>14 (20)</td>
<td>36 (52)</td>
</tr>
</tbody>
</table>

The hybridization gap. The interband transitions were related to a strong peak seen at 600 cm$^{-1}$ which has less spectral weight in our experiments. Besides the understandable differences between different experimental sets, the origin of such large spectral weight could be due to an overestimation of the reflectivity in the visible range (where we used ellipsometry). To check this supposition, we have performed KK using our own reflectivity data and the reflectivity from Ref. [129] above 6000 cm$^{-1}$. The result is presented as the gray dotted line in Fig. 5.4(a). Such procedure gives more spectral weight at around 600 cm$^{-1}$. Therefore, the shoulder at 250 cm$^{-1}$ most probably corresponds to transitions across $\Delta$. This assignment is further supported below when we discuss the properties of $\epsilon_1(\omega)$.

5.2.3 Dielectric Function and Plasma Oscillation of the Condensate

The development of the hybridization gap can also be seen in the real part of the dielectric function at low frequencies (Fig. 5.6). As the temperature is lowered, $\epsilon_1(\omega)$ changes from purely metallic (monotonically decreasing) to a region with a maximum. At the lowest measured temperature, in the Co and Ir compounds, it even has two extra zeros whose values are given in Table 5.1. This behaviour shows the definitive establishment of the coherent state, a well known effect [17] that has been experimentally seen only recently [130]. The lowest zero, $\omega^*$, may be thought of as the heavy fermion plasma mode [131] while the second one, $\omega_1$, comes from the contribution of the interband transitions to $\epsilon_1(\omega)$. Since these transitions have a threshold energy $\Delta$, $\omega_1$ gives an estimate of the value of the hybridization gap. The shoulders seen at $\sim250$ cm$^{-1}$ in the Co and Ir compounds are above the gap and therefore most likely correspond to transitions across the gap. The dielectric function of CeRhIn$_5$, though it shows a maximum at 8 K, has not zero crossings indicating that, in contrast to the other compounds, the
5.2. **OPTICAL PROPERTIES OF CEMIN₅ (M = CO, RH, IR)**

![Image of Figure 5.6](attachment:figure_5.6.png)

**Figure 5.6:** Real part of the dielectric function in the infrared. The arrows indicate the zero crossings of $\epsilon_1(\omega)$. Insets: Temperature dependence of $\epsilon_1(\omega)$ at selected frequencies: 100 (triangles) and 180 (circles) cm$^{-1}$. 

- **CeCoIn₅**
- **CeRhIn₅**
- **CeIrIn₅**
coherent state is not completely formed. We interpret this phenomenon as the well known competition between magnetic ordering and the formation of the correlated state. Those systems that form a magnetically ordered state, usually present a smaller heavy fermion character[125]. To get more insight about this point, we analyze our results with the generalized Drude formulation (Eq. 2.24):

\[
\sigma(\omega) = \frac{\omega_p^2}{4\pi} \frac{1}{1/\tau(\omega) - i \omega m^*(\omega) / m}
\]

where we used \(\omega_p\) corresponding to the effective number of electrons, \(N_{eff}\), at 2000 cm\(^{-1}\) and given in Table 5.1. The obtained frequency dependent mass, \(m^*(\omega) / m\), is plotted in the insets of Fig. 5.4. The increase of the effective mass is evident at low frequencies as soon as the temperature is lowered below \(T_{coh}\). At the lowest measured frequency, the mass enhancement depends on the sample. However, from a fit to reflectivity, ellipsometry and DC conductivity, we estimate similar mass enhancements at \(\omega \to 0\). Analogous results are obtained if the effective mass is calculated using spectral weight arguments (see Table 5.1) \(^\dagger\). The difference between them is the energy range where the mass enhancement occurs, being much smaller for CeRhIn\(_5\). In contrast, specific heat measurements [116, 117, 118] indicate (in the normal state) \(\gamma = 300, 400, \) and 750 mJ/(mol K\(^2\)) for Co, Rh, and Ir, respectively. At least for CeRhIn\(_5\), as indicated by measurements of the de Haas-van Alphen experiment [139] and of the specific heat in magnetic field [134], this value of \(\gamma\) seems to be overestimated as the specific heat contains large contributions from magnetic interactions and not only from strong interactions. Another way to see the smaller heavy fermion character of CeRhIn\(_5\) is by studying a simple relation obtained from the calculation of the dielectric function for the Anderson lattice [131]:

\[
\omega^* = 6(1 + n_f / n_c)T^* \tag{5.1}
\]

where \(n_c\) and \(n_f\) are the density of conduction and f-electrons. Since it is expected that these two quantities do not change in the CeMIn\(_5\) (M = Co, Rh, Ir) group\(^\ddagger\) and given the values found for \(\omega^*\), the characteristic temperature \(T^*\) should be approximately the same for CeCoIn\(_5\) and CeRhIn\(_5\) but markedly decreased for CeRhIn\(_5\). If we identify \(T_{coh}\) with \(T^*\), this is indeed the case (CeRhIn\(_5\) does not show a maximum in its resistivity but we have taken \(T_{coh}\) as the inflection point; see Fig. 1.10). From the study of the specific heat and the magnetic susceptibility [127, 128], different values of \(T^*\) were obtained (Table 5.1) contradicting our

\(^\dagger\)The mass enhancement is the ratio between the integrated spectral weights of the broad Drude peak at room temperature and the narrow peak at low temperatures. The limit of the integration was 2000 cm\(^{-1}\) for the room temperature peak. For the narrow peak the limits were 55, 35, and 60 cm\(^{-1}\) for the Co, Rh, and Ir compounds, respectively.

\(^\ddagger\)From a naive point of view this is expected since Co, Rh and Ir are isoelectronic and therefore no change in \(n_c\) is expected. As an experimental confirmation we remit to Table 5.1 where \(N_{eff}\) at 2000 cm\(^{-1}\) is shown.
observation of a completely settled coherent state in CeIrIn$_5$ at 8 K. It seems that more sophisticated calculations are needed to understand the various energy scales involved and how they impact the spectral weight transfer. Moreover, this effect in CeIrIn$_5$ also argues against some results that suggest that the f-electrons in this compound are more localized than those in CeCoIn$_5$. This latter point has been rather controversial [135].

5.2.4 Spectral Weight

The last point we want to discuss is the spectral weight contained by $\sigma_1(\omega)$ which was defined in Eq. 2.8 and we reproduce here:

$$N_{\text{eff}}(\omega) = \frac{mV}{\pi e^2} \int_0^{\omega} \sigma_1(\omega')d\omega'$$

The volume $V$ was calculated from the lattice parameters given in References [116], [117], and [118]. $N_{\text{eff}}$ is depicted in Fig. 5.7 and the temperature dependences at 400 and 2000 cm$^{-1}$ are shown in its insets. For comparison purposes, the DC resistivities [116, 117, 118] are also shown in the insets. When the hybridization gap develops, spectral weight is removed from the low frequency part as evinced, for example, by the behavior of $N_{\text{eff}}$ at 400 cm$^{-1}$. The spectral weight does not start recovering immediately above the gap but eventually does at an energy range much larger than the gap itself, $\sim$2000 cm$^{-1}$ (0.25 eV). Other Kondo systems show similar behavior. In particular, an interesting case is FeSi, where the spectral weight lost during the formation of the Kondo insulator state is transferred to an energy range on the order of several eV (see Chapter 4). The difference between the energies where the recovery of spectral weight takes place seems to be related with the nature of the local moments, $d$ versus $f$-electrons. While the $f$-electrons form extremely narrow bands, the $d$-electrons form rather broad bands.

5.3 Optical Properties of LaRhIn$_5$

A common practice in the study of Kondo lattices is to replace the magnetic centers by a non-magnetic element. In the case of cerium-based compounds this is achieved by substituting it with lanthanum. In the CeMIn$_5$ (M = Co, Rh, Ir) system this procedure has proven to be very useful as the continuous substitution of Ce by La does not change important characteristics as the crystalline electric field or the Kondo coupling [127]. In this work we have measured the reflectivity (at different temperatures) and ellipsometry (at room temperature) of a single crystal of LaRhIn$_5$. The experimental results are summarized in Fig. 5.8.

Figure 5.8a and its inset show the reflectivity of this compound. In contrast with the magnetic lattices studied in the previous section, the reflectivity increases when lowering the temperature. This effect is common in metals due to the
Figure 5.7: Spectral weight of $\sigma_1(\omega)$. Insets: Temperature dependences of $\Delta N_{\text{eff}}$ at 400 (circles) and 2000 (triangles) cm$^{-1}$, and DC resistivities (gray line) from Refs. [116, 117, 118].
5.3. OPTICAL PROPERTIES OF LARHIN$_{5}$

Figure 5.8: Results of the optical spectroscopy performed in a single crystal of LaRhIn$_{5}$. (a) Measured reflectivity at several temperatures and room temperature reflectivity calculated from ellipsometry. Inset: Reflectivity below 1000 cm$^{-1}$. (b) Real part of the optical conductivity. Inset: Phase of the complex conductivity below 1000 cm$^{-1}$. (c) Real part of the dielectric function. Inset: Expanded view of $\epsilon_1(\omega)$.
reduction of the scattering rate. Both the real parts of the optical conductivity (Fig. 5.8b) and of the dielectric function (Fig. 5.8c) show that indeed the scattering rate is reduced. This can be seen from the fact that, at low frequencies, both decrease with decreasing temperature. In particular, $\epsilon_1(\omega)$ remains metallic down to the lowest measured temperature without the appearance of the maximum seen in the magnetic counterpart. Finally, the inset of Fig. 5.8b shows the quantity $\frac{1}{2} - \frac{\arg[\sigma(\omega)]}{\pi}$ which above above $\sim 250 \text{ cm}^{-1}$ reaches a plateau at around 0.1. According to the discussion in §2.4.2, this signals a departure from the Drude model. In the context of Eq. 2.20 this would mean that $\eta = 0.1$.

We have indeed fit reflectivity and ellipsometry data with the above mentioned equation. The results are depicted in Fig. 5.9. It is important to mention that, since the fit at different temperatures gives a large value for $\Gamma$, this parameter
5.3. OPTICAL PROPERTIES OF LARHIN$_5$

![Diagram showing optical properties](image)

**Figure 5.10:** (a) Effective number of carriers. (b,c) Frequency dependent mass and scattering rate.
was kept constant at all temperatures. The results indicate that both, the plasma frequency, \( \omega_p \), and the exponent \( \eta \) do not show a strong temperature dependence. Moreover, the value of the later is \( \sim 0.1 \) as expected from the phase of the optical conductivity. In contrast, parameter \( \gamma \) has a strong temperature dependence. The situation is similar to what was found in MnSi.

For LaRhIn\(_5\) we have also calculated the spectral weight and performed the extended Drude analysis. The former is shown in Fig. 5.10a where we have used the lattice parameters reported in Ref. [138]. As it happens in CeMIn\(_5\), after a sharp raise, \( N_{\text{eff}} \) exhibits a plateau and reaches \( \sim 1.2 \) at 2000 cm\(^{-1}\). At the same frequency, \( N_{\text{eff}} \) is \( \sim 1.8 \) in CeRhIn\(_5\) (see Table 5.1), which is consistent with the fact that cerium has one more electron than lanthanum.

The results of the extended Drude analysis are given in Figures 5.10b-c. The fact that both, the mass enhancement and the scattering rate are not constant, indicate a strong deviation from the Drude response as it was concluded in the previous analysis of the phase of the optical conductivity. The extrapolation (dotted lines in 5.10b) gives an mass enhancement of 3. This is \( \sim 5 \) times smaller than the mass enhancement found in CeRhIn\(_5\). Similar ratios have been found when comparing results of de Hass-van Alphen and heat capacity experiments [18]. The former gives a ratio of 7-9 for the cyclotron masses in the main bands. Heat capacity results, instead, give a ratio of \( \sim 9 \) between the \( \gamma \)-coefficients. The frequency dependent scattering rate depicted in Fig. 5.10c is quasi-linear at low frequencies. In comparison, the DC resistivity is linear from 300 down to \( \sim 20 \) K where it saturates[137]. This indicates a strong electron-phonon coupling which naturally leads to deviations from the Drude formulation[39].

### 5.4 Conclusions

In conclusion, we have presented optical measurements on one of the recently most studied families of heavy fermion systems, CeMIn\(_5\) (M = Co, Rh, Ir). We have shown that in all the compounds presented here, the spectral weight is recovered in the same frequency range of about 0.2 eV which is larger than the hybridization gap. Moreover, we can directly see how the coherent state is quenched by a competing phenomenon: antiferromagnetism.

Finally, we have also performed optical experiments in one of the non-magnetic counterparts of this family, LaRhIn\(_5\). None of the characteristic features of the heavy fermion systems has been found in this material. However, we were able to distinguish a strong deviation from the Drude formulation. Since the DC resistivity is linear, this can be an effect of a strong phonon-electron coupling.