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# Pressure evolution of $f$ electron hybridized state in $CeCoIn_5$ studied by optical conductivity

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**Abstract.** Optical conductivity $\sigma(\omega)$ of $CeCoIn_5$ has been measured under high pressure to 8 GPa and at low temperatures to 6 K, to study the pressure evolution of the conduction ($c$)-$f$ electron hybridized state near the Fermi level. At ambient pressure, $CeCoIn_5$ is a heavy fermion superconductor with $T_c$=2.3 K, and has moderately strong $c$-$f$ hybridization. $\sigma(\omega)$ at ambient pressure shows a marked infrared peak due to optical excitations involving the $c$-$f$ hybridized state. With increasing pressure, the infrared peak becomes broader, and its center shifts to higher energy. This result indicates that the large density of states of the $c$-$f$ hybridized state becomes broader with increasing pressure, and that the peak of the density of states shifts away from the Fermi level. Althouth such pressure evolution of the $c$-$f$ hybridized state had been widely assumed on the basis of theoretical consideration, the present optical result demonstrates it clearly and directly.

## 1. Introduction

Heavy fermion (HF) compounds, which are typically intermetallic compounds containing Ce or Yb, have attracted a lot of attention due to their interesting physical properties. In HF compounds, for example, a hybridization between the conduction electrons and the otherwise localized $f$ electrons, which have strong correlation, leads to the formation of heavy fermions (quasiparticles with large effective mass). In addition, duality between delocalized and localized characteristics has been observed in their physical properties, which have been studied by a wide range of experimental techniques. In particular, their physical properties under high pressure are quite interesting since external pressure can tune the degree of localization and delocalization in many HF compounds [1]. The simplest $f$ electron configuration in a HF compound is $f^1$ for $Ce^{3+}$. Since a $Ce^{3+}$ ion has larger ionic radius than a $Ce^{4+}$ ion with $f^0$ configuration, an external pressure generally drives the configuration toward larger valence value (from $Ce^{3+}$ to $Ce^{4+}$), hence transferring the electron from $f$ orbital to conduction band. In the context of the periodic Anderson model, this is equivalent to increasing the hybridization between the conduction ($c$) and $f$ electrons, and hence increasing the Kondo temperature of the system.

In this work, we have measured the optical conductivity [$\sigma(\omega)$] of $CeCoIn_5$ under high pressure to 8 GPa in order to study the pressure evolution of its microscopic electronic structures near the Fermi level ($E_F$). $CeCoIn_5$ is a well known HF compound which shows a superconductivity with $T_c$=2.3 K [2]. Just above $T_c$, its electronic specific coefficient is about 250 mJ/K$^2$mol


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[2], which indicates a moderately strong $c$-$f$ hybridization in this compound. Upon applying external pressure, $T_c$ increases to about 2.5 K at 1.5 GPa, but then decreases with further pressure [3, 4]. Measured $\sigma(\omega)$ of $CeCoIn_5$ at ambient pressure and at low temperature showed a marked peak centered near 600 $cm^{-1}$ (75 meV) [5]. This infrared peak has been interpreted as arising from optical excitations involving the $c$-$f$ hybridized state. Our present result shows that $\sigma(\omega)$ of $CeCoIn_5$ is strongly influenced by external pressure. With increasing pressure to 8 GPa, the above mentioned infrared peak is significantly broadened, and is shifted to higher energy. These results suggest that, with increasing pressure, the density of states (DOS) of $c$-$f$ hybridized state becomes broader and the hybridization actually becomes stronger. Although such properties have been commonly assumed in the discussion of HF compounds under high pressure, they had not been directly observed by a spectroscopic experiment.

## 2. Experimental Techniques

Optical conductivity spectra of $CeCoIn_5$ were derived from the measured reflectance spectra [$R(\omega)$]. The samples used were single crystals grown by the self flux method [2]. As-grown, flat surfaces showing specular reflection were used for $R(\omega)$ measurements without mechanical polishing. $R(\omega)$ at ambient pressure was measured over a wide photon energy range between 10 meV and 30 eV [6]. $\sigma(\omega)$ was derived from the measured $R(\omega)$ using the standard Kramers-Kronig analysis [7, 8]. $R(\omega)$ spectra at high pressure up to 8 GPa were measured with a diamond anvil cell (DAC) in the photon energy range between 20 meV and 1.1 eV [11, 12]. The surface of a thin sample was closely placed on the culet surface of the diamond anvil. A gold film was also mounted in the DAC with the sample, and was used as the reference of reflectance. Glycerin was used as the pressure transmitting medium [9, 10]. To overcome the difficulty of accurately measuring $R(\omega)$ within the limited sample space of DAC, synchrotron radiation was used as a bright infrared source at the beam line BL43IR of SPring-8 [11, 12]. $\sigma(\omega)$ at high pressure was derived from the $R(\omega)$ measured with DAC using a modified Kramers-Kronig analysis, which took into account the influence of the large refractive index of diamond on the measured $R(\omega)$ [13]. More details of the infrared measurements under high pressure have been described elsewhere [11, 12].

## 3. Results and Discussion

Figure 1 shows the measured $\sigma(\omega)$ of $CeCoIn_5$ at ambient pressure and at different temperatures. The obtained results are very similar to the previously reported ones [5]. At room temperature, $\sigma(\omega)$ rises with decreasing photon energy, which represents the so-called Drude response of free carriers in a metal [7, 8]. With decreasing temperature, however, the Drude response is gradually suppressed, and a marked peak appears and grows near 0.05 eV. Note that, since this compound is a metal, its dc conductivity ($\sigma_{dc}$) increases with cooling, in contrast to the observed decrease of $\sigma(\omega)$. These contrasting temperature dependences of $\sigma_{dc}$ and $\sigma(\omega)$ are characteristic of HF compounds, as previously discussed [14]. At 8 K, $\sigma_{dc}$ reaches about $10^5$ $\Omega^{-1}cm^{-1}$ [2], which is indicated by the red dot on the vertical axis of Fig. 1(a). This value is about ten times larger than $\sigma(\omega)$ at the lowest measured photon energy. Namely, there should be a very narrow and strong peak in $\sigma(\omega)$ below the lower energy limit of our measurement, as indicated by the broken curve in Fig. 1(a). This narrow peak is due to the Drude response of heavy quasiparticles formed at low temperature, and has actually been observed for some HF compounds using microwave technique [14, 15]. Regarding the infrared peak, on the other hand, a similar peak in $\sigma(\omega)$ has been observed for many other Ce and Yb based HF compounds [16, 17, 18, 19]. The infrared peak energy is varied from one compound to another, but it is generally observed in the range between 0.05 and 0.3 eV. The microscopic origin for the infrared peak has been discussed by many authors, both in terms of simple $c$-$f$ hybridization bands [16, 17, 18, 19] and more detailed band structure calculations [20, 21, 22]. It is now widely believed that the infrared peak results

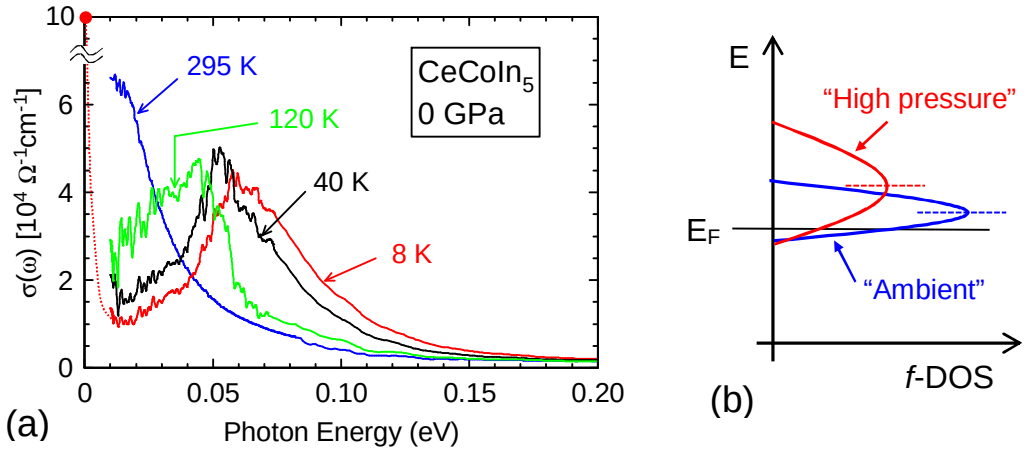



**Figure 1.** (a) Optical conductivity $[\sigma(\omega)]$ of $CeCoIn_5$ at ambient pressure and at several temperatures. The red dot on the vertical axis indicates the dc conductivity of $CeCoIn_5$ at 8 K [2], and the red broken curve is guide to the eye. (b) A schematic illustration of the $f$-DOS, namely the $f$ component in the density of states of the $c$-$f$ hybridized state near the Fermi level ($E_F$). The broken lines indicate the peak position of the $f$-DOS. As discussed in the text, under high pressure, the $f$-DOS becomes broader, and the $f$ level is shifted away from $E_F$.

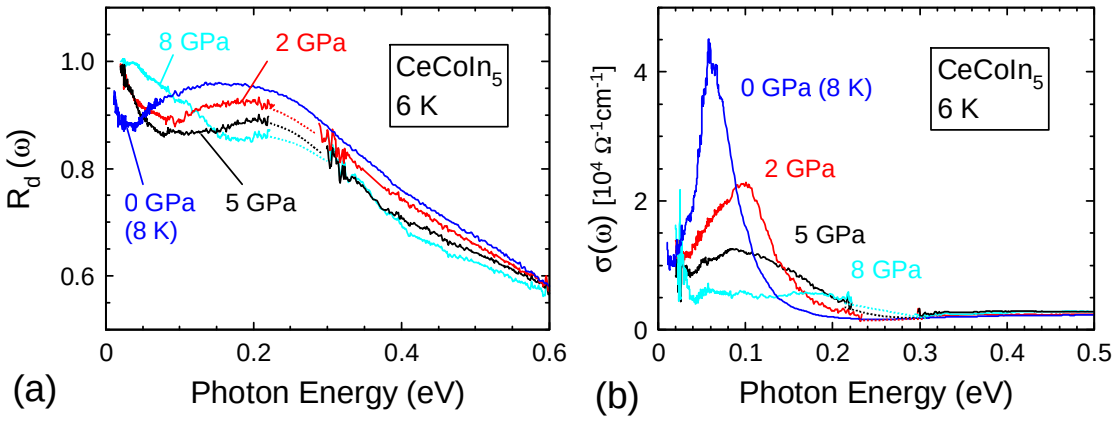



**Figure 2.** Optical reflectance $[R_d(\omega)]$ (a) and conductivity $[\sigma(\omega)]$ (b) of $CeCoIn_5$ measured at high pressure and at low temperatures. The broken curves show the interpolations for the spectral range that could not be measured due to strong absorption by the diamond anvil.

from optical excitations from or to a large DOS of the $c$-$f$ hybridized state near $E_F$. In the case of a Ce compound, as in the present case, the $4f$ shell is almost empty with only one or less electron per Ce in average. Hence, as sketched in Fig. 1(b), the $f$ component of the large DOS is mostly unoccupied, and the peak of the DOS is located above $E_F$. (In a Yb compound, in contrast, it is mostly occupied and the peak is located below $E_F$.) Hence, the infrared peak in $\sigma(\omega)$ should correspond to optical excitation of electrons from occupied states below $E_F$ to unoccupied states in the large DOS above $E_F$. In the present case of $CeCoIn_5$, the development of the infrared peak centered at $\sim 0.06$ eV indicates that the sharp DOS of the $c$-$f$ hybridized state is located within $\sim 0.1$ eV above $E_F$.

Figures 2(a) and 2(b) show the optical reflectance $R_d(\omega)$ and optical conductivity $\sigma(\omega)$ of $CeCoIn_5$, respectively, measured at 6 K and at external pressures of 2, 5, and 8 GPa. Note

that the part of the spectra indicated by the broken curves (0.22-0.3 eV) could not be measured due to strong absorption by the diamond anvil. [This part of $R_d(\omega)$ spectra was smoothly interpolated to perform the Kramers-Kronig analysis.] Note also that $R_d(\omega)$ was measured at the sample/diamond interface, unlike the usual case of sample/vacuum interface, which was taken into account in the data analysis [13]. It is seen that both $R_d(\omega)$ and $\sigma(\omega)$ spectra are strongly influenced by the external pressure. Namely, the dip in $R_d(\omega)$ located below 0.1 eV at 0 GPa is shifted to higher energy with increasing pressure, and it is also broadened. Accordingly, the infrared peak in $\sigma(\omega)$ is shifted to higher energy and broadened. These pressure evolutions of the infrared peak should be closely related with those of the $f$-DOS (the $f$ component in the DOS of the $c$-$f$ hybridized state). Therefore, as sketched in Fig. 1(b), the present experimental result suggests that the sharp $f$-DOS at ambient pressure is broadened with increasing pressure, and that the peak of $f$-DOS is shifted upward in energy. In the literature on the physical properties of HF compounds under high pressure, such pressure evolution of the $c$-$f$ hybridized state has been often assumed on the basis of theoretical expectations. Namely, the upward shift of the $f$-DOS relative to $E_{\rm F}$ is expected since the filling of the $f$ shell should become smaller as the pressure drives a crossover from $Ce^{3+}$ ($f^1$) to $Ce^{4+}$ ($f^0$) as discussed in Introduction. In addition, the $f$-DOS is expected to become broader since the hybridization and the Kondo temperature are also expected to increase with pressure. In the present result, these behaviors are clearly observed in the form of energy dependent optical conductivity, which can also be regarded as the charge excitation spectra.

In Fig. 2, the spectral weight of the infrared peak, namely the area of the peak in $\sigma(\omega)$, is apparently decreasing with increasing pressure. The spectral weight of a peak in $\sigma(\omega)$ is proportional to the effective electron density $N^*$ (electron density divided by effective mass), contributing to the optical excitations causing the peak [7, 8]. Therefore, the spectral weight should be conserved with pressure if $N^*$ contributing to the peak is unchanged. The "missing" weight is presumably transferred to the spectral ranges outside our measurement. As already mentioned in connection with Fig. 1(a), there should be a narrow and strong Drude peak due to heavy quasiparticles below the measurement range of our study. Since $\sigma_{\rm dc}$ at low temperature significantly increases with pressure [4], the narrow Drude peak should also gain more spectral weight with pressure. Therefore, it is likely that a portion of the missing spectral weight has been transferred to the Drude peak, but an explicit study of the Drude response under pressure is technically difficult. It is interesting to note that, in the ambient pressure data of Fig. 1(a), the spectral weight of the infrared peak is almost conserved with temperature below 120 K. Namely, in terms of the spectral weight, the temperature evolution of the infrared peak at ambient pressure is qualitatively different from the pressure evolution at low temperature. It is unlikely that the decrease of spectral weight is due to the modified Kramers-Kronig analysis, since the data at different pressures were treated in exactly the same way. The limited spectral range of this study might also have played some role in the decreasing spectral weight. However, we believe that the high-energy shift and broadening of the infrared peak are intrinsic properties of this system since they were reproducible under repeated measurements, and the pressure evolutions of the data in the far infrared and mid-infrared ranges were consistent with each other.

As mentioned in Introduction, similar infrared peak in $\sigma(\omega)$ has been observed for many Ce and Yb-based HF compounds that have different degree of $c$-$f$ hybridization. The observed peak energy varies from one compound to another. It has been found, however, that the peak energy is roughly proportional to the hybridization energy of these compounds [19]. Therefore, the present result of pressure-induced peak shifts to higher energy may be viewed as the direct evidence for a pressure-induced increase of $c$-$f$ hybridization, with information about how the energy-dependent $f$-DOS changes with pressure. For future work to perform a more quantitative analysis of the $c$-$f$ hybridized state under high pressure, a more detailed model based on the

microscopic electronic structure should be developed.

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