Optical response of $PrRu_4P_{12}$ due to metal-insulator transition

Masato Hayashi[a],Masaya Nakayama[a] ,Takao Nanba[a], Itimin Shirotani[b], and Chihiro Sekine[b]

a Graduate school of Science and Technology, Kobe University, Nada-ku,
Kobe 657-8501, Kobe,Japan

b Muroran Institute of Technology, 27-1, Mizumoto,Muroran 050-0071, Japan

$PrRu_4P_{12}$ and $CeRu_4P_{12}$ are ones of ternary metal phosphides with the skutterudite structure ($CoAs_3$-type) which is represented as RT_4P_{12} (R=rare earth element and T=transition metal). Recently, their stable compounds have been successfully synthesized using a wedge-type cubic anvil high pressure apparatus under a high pressure of 4 GPa and high temperature of 1100 °C[1] Most of them show an interesting physical properties at low temperature. According to the electric resistivity data, $CeRu_4P_{12}$ and $CeFe_4P_{12}$ are a semiconductor [1,2], $LaRu_4P_{12}$ shows a superconductivity, and $PrRu_4P_{12}$ show a metal-insulator transition with Tc=60K [3].

After the success of the synthesis, many experiments has started on these compounds but the optical measurements has not yet been done. We measured the reflection spectrum in order to know the electronic structure close to the Fermi energy level. In the present report the results of $PrRu_4P_{12}$ and $CeRu_4P_{12}$ are presented.

The temperature dependence of the optical reflection spectra of $PrRu_4P_{12}$ and $CeRu_4P_{12}$ were measured in the energy region of 5 meV-4 eV. A Michelson type of interferometer, Bruker 66v, was used with a suitable beam splitter in each available region combined together with a Si bolometer, a mercury-cadmium-telluride and a silicon photo-diode detector, respectively. The energy resolution was 4 cm^{-1} in the infrared region. The whole reflection spectrum at each temperature was obtained by connecting reflection spectra at different energy regions. The ordinate of the spectrum was calibrated by measuring the reflectivities by a few of He-Ne and argon ion laser lines. Finally the optical conductivity spectrum ($\sigma(\omega)$) was obtained from a Kramers-kronig transformation of the reflectivity spectrum.

Fig.1 shows the measured reflection (a) and the optical conductivity spectra (b) of $CeRu_4P_{12}$ at 300 K (dashed line) and 10 K (solid line). Both spectra showed a semiconductor-like behavior. We can see many phonon lines in the infrared region and the onset of the interband transition as the abrupt rise in the intensity of σ-spectra around 1000 cm^{-1} at a room temperature and 10 K. Fig.2 shows the reflection (a) and the σ spectra (b) of $PrRu_4P_{12}$ at 80 K (dashed line) and 10 K (solid line). The reflection and the σ spectra of $PrRu_4P_{12}$ at 80 K give a metallic profile. The abrupt rise in the reflection spectra below 2500 cm^{-1} corresponds to a so-called plasma frequency due to the collective motion of the free carriers. On the other hand, the reflection spectrum at 10 K showed a definite decrease in the intensity in the region below 1000 cm^{-1} although the position of the onset in the reflection does not change except the sharpening of the dip structure at 2500 cm^{-1}. The overall decrease in the intensity of the reflectivity means the transition to an insulating state from a metallic. In the σ spectra, the intensity around 200 cm^{-1} increases so as to compensate the decrease the intensity below 100 cm^{-1}.

The electronic configuration of $CeRu_4P_{12}$ is $Ce^{4+}[(Ru_4)^{8+}(P_{12})^{12}]^{4+}$ and then the outer electron orbit of Ru^{2+}ion is $(4d)^6$. This configuration gives a semiconductor character because the lower energy t_{2g} state due to the octahedral crystalline field splitting is fully occupied and the upper e_g state is unoccupied. On the other hand, if the valence of the Pr ion of $PrRu_4P_{12}$ is Pr^{3+}, the valence of Ru ion has mixed valence of Ru^{3+}:$(4d)^5$ and Ru^{2+}:$(4d)^6$. The $(4d)^5$ configuration gives the partially unoccupied state of the t_{2g} state of Ru 4d orbit which gives rise to the metallic properties of $PrRu_4P_{12}$("valence fluctuation model"). However, the volume anomaly due to the metal(Pr^{3+})-insulator(Pr^{4+}) transition at 60 K has not been observed by the X-ray diffraction measurement. On the other hand, recent band calculation of $CeFe_4P_{12}$ pointed out the possibility of the gap formation due to the hybridization of the 4f state (Ce ion) with the 4d state (Ru ion) close at the Fermi level [4]. The

peak at 200 cm^{-1} in the σ spectra of PrRu$_4$P$_{12}$ at 10 K may corresponds to the allowed transition between the mixed 4f-4d state.

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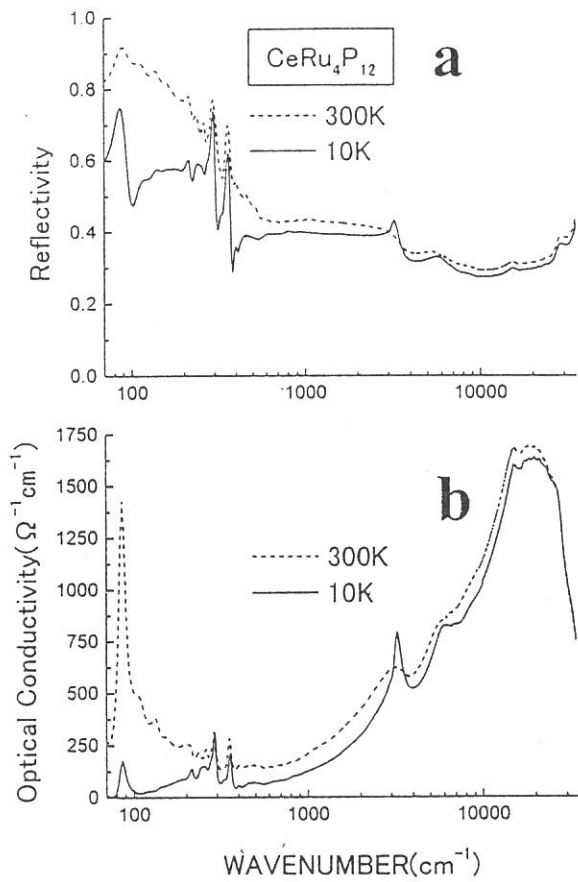[4] L.Nordström and D.J.Singh, Phys.Rev.**B53**, (1996)1103.

Fig.1   Reflection (a) and optical conductivity spectra (b)
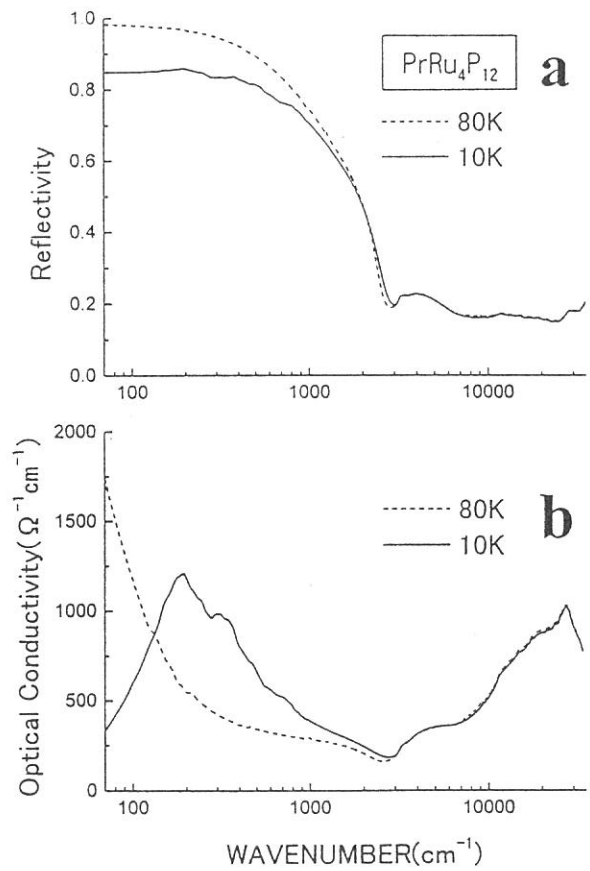   of CeRu$_4$P$_{12}$ at 300 K (dashed line) and 10 K (solid line).

Fig.2   Reflection (a) and the σ spectra (b) of PrRu$_4$P$_{12}$
        at 80 K (dashed line) and 10 K (solid line).

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Reflection Measurements of Secondary Battery Substances $Li_{1-x}Ni_{1+x}O_2$ in the Millimeter Wave Region

Hitoshi OHTA, Shunsuke ONO, Atushi UEDA, Takao NANBA, Atushi HIRANO[*]
and Ryoji KANNO[*]

Department of Physics, Faculty of Science, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501
[*]*Department of Chemistry, Faculty of Science, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501*

Recently $LiNiO_2$ has attracted much attention as an electrode material in Li ion secondary batteries. Although the composition of $LiNiO_2$ is very sensitive to the synthesis condition, especially the sintered temperature, and it can be easily lead to a decomposition of $Li_{1-x}Ni_{1+x}O_2$ which degrades the charge and discharge characteristics, Kanno *et al.* succeeded in synthesizing nearly stoichiometric $LiNiO_2$ and controling the concentration x.[1] We started our investigation to obtain the information about the diffusive motion of Li^+ ions in $LiNiO_2$ by observing "ionic plasmon" in the millimeter wave region because the mass of Li^+ ion is much heavier than that of electron. As we reported before,[2] we succeeded in observing an increase in a reflectivity of $LiNiO_2$ towards a low energy side in the millimeter wave region above 300K. In this study we tried to analize the data and also tried the measurement of non-stoichiometric sample to compare with the stoichiometric sample.

The reflection measurements of x=0.01 sample sintered at 650°C (sample A) and x=0.05 sample sintered at 850°C have been performed in the spectra region from 6 to 60 cm^{-1} using the beam line BL6A1 of UVSOR. For the measurement below 22 cm^{-1}, low pass filter was used. The temperature was changed from 79 K to 380 K for both samples. The gold plate was used as a reference and InSb detector was used as a detector. Figures 1 and 2 show our results for samples A and B. First we tried to analyze our data by simple Drude model but it turned out to be too simple to interpret our results. Therefore we employed the phenomenological model by Bruesch *et al.* [3] The fitted results are shown by dashed lines in Fig. 1 and the obtained plasma frequency turned out to be about 80 cm^{-1}. Therefore we need more measurements in higher wavenumber region in order to perform more accurate analyses. The temperature dependence of sample B shows similar behavior but higher reflectivity and the relaxation time in sample B seems to be shorter. More detailed x dependence measurements are still underway.

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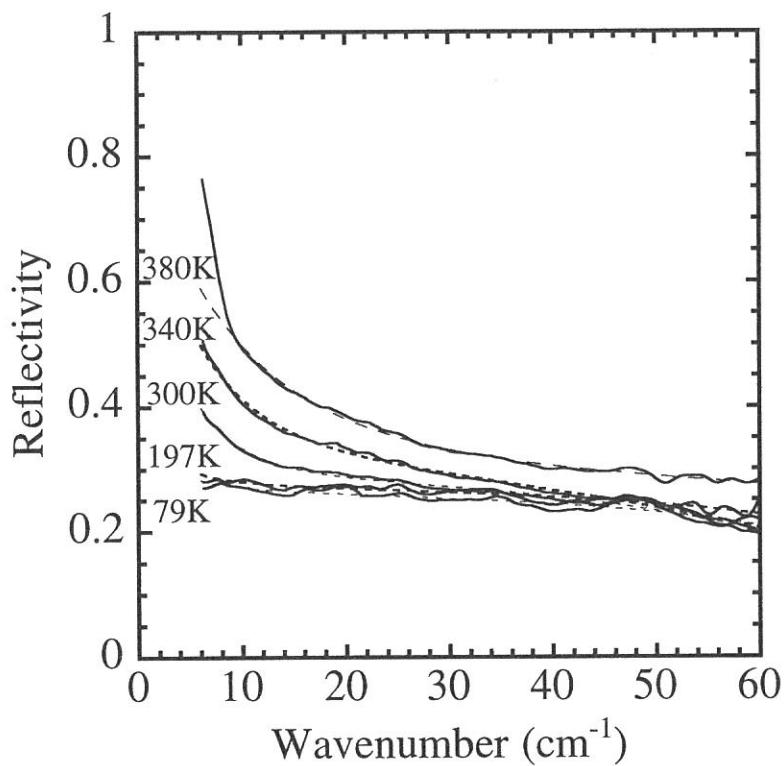[3] Bruesch *et al.*: phys. stat. sol. (a) **31** (1975) 217.

Fig.1 Reflection spectra of $Li_{1-x}Ni_{1+x}O_2$ sintered at 650℃ (sample A). x is about 0.01. Dashed lines are fitting curves.
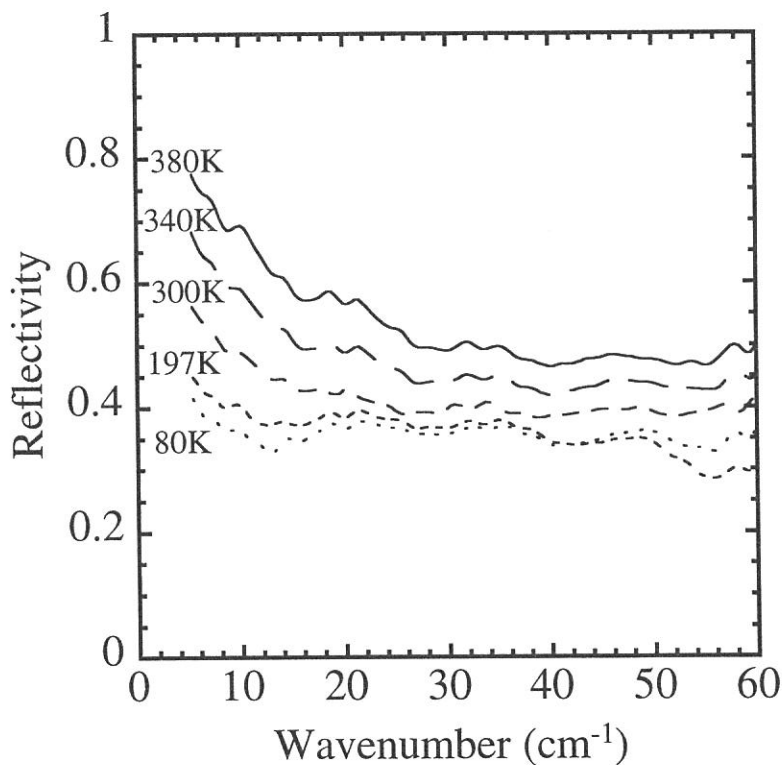
Fig.2 Reflection spectra of $Li_{1-x}Ni_{1+x}O_2$ sintered at 850℃ (sample B). x is about 0.05.

Electronic structure in magnetic ordered state of CeSb studied by magneto-optical spectroscopy in the infrared region

Shin-ichi Kimura[1], Hideaki Kitazawa[2], Giyu Kido[2], and Takashi Suzuki[3]

[1]Graduate School of Science and Technology, Kobe University, Nada-ku, Kobe 657-8501
[2]Physical Properties Division, National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, 305-0047
[3]Institute for Solid State Physics, The University of Tokyo, 7-22-1 Minato-ku, Tokyo 106-8666

Materials in the magnetic ordered state shows the diversity of the physical properties in comparison with the normal state. Since the electronic structure in the ordered state should reflect the physical properties, the investigation of the electronic structure gives much useful information of the origin of the physical properties.

Cerium monopnictide (CeX; X = N, P, As, Sb, Bi) has complex magnetic phase diagram. In CeX series, CeSb is the material which has been studied very much. The famous neutron diffraction experiment has been done by Rossat-Mignod et al. and the complex magnetic phase diagram of 16 phases of CeSb was observed.[1] However the origin of the complex magnetic phase has been unclear yet. Our purpose is to understand the origin of the complex magnetic phase from the electronic structure in the magnetic ordered state of CeSb using optical reflectivity and magnetic circular dichroism measurement under magnetic field in the infrared region.

The CeSb sample was grown by a Bridgman method of a high-frequency furnace. The sample size for the optical measurement is about 4 mmϕ and 1 mm thickness. The sample was scraped along (100) plane in helium atmosphere and was mounted a closed cycle helium cryostat.

The magneto-optical experiment was done by using the infrared magneto-optical apparatus.[2] The measuring parameters of temperature, magnetic field and photon energy are 6.5 – 30 K, 0 – 6 T, and 0.05 – 2 eV, respectively. The optical measurement was done along the (100) plane and the magnetic field was applied to the <100> direction.

In this study, reflectivity spectra under magnetic field with unpolarized light (MR) and magnetic circular dichroism spectra of reflectivity with circularly polarized light (MCDR) were measured in the energy range of 0.05 – 2 eV. The optical conductivity spectra ($\sigma_{xx}(\omega, T, H)$) and the magnetic circular dichroism optical conductivity spectra ($\sigma_{\pm}(\omega, T, H)$) were obtained by the Kramers-Kronig transformation of the MR and MCDR spectra, respectively. Here, ± indicates the different selection rule of the magnetic quantum number of ±1. Below, the analysis is done by using the σ and $\sigma_{\pm}$ spectra.

Figure 1 indicates the temperature dependence of reflectivity spectrum from 6.5 to 30 K at 3 T. Above 20 K, the magnetic phase is assigned to be para-phase. The spectrum is very similar to those measured by Kwon et al.[3] and Pittini et al.[4] The spectra below the temperature change very much. The boundaries of the different spectra indicate the temperature of the magnetic or structural phase transition.

The parameters of temperature and magnetic field at which the MR spectra were measured are shown in Fig. 2. The same mark is the point of the same spectrum.

The boundary of the different marks indicates the phase transition point. The boundary is in good agreement with the magnetic phase diagram which was obtained by using the neutron scattering.[1] Therefore the result indicates that we can get the information of the magnetic phase transition from the MR spectra.

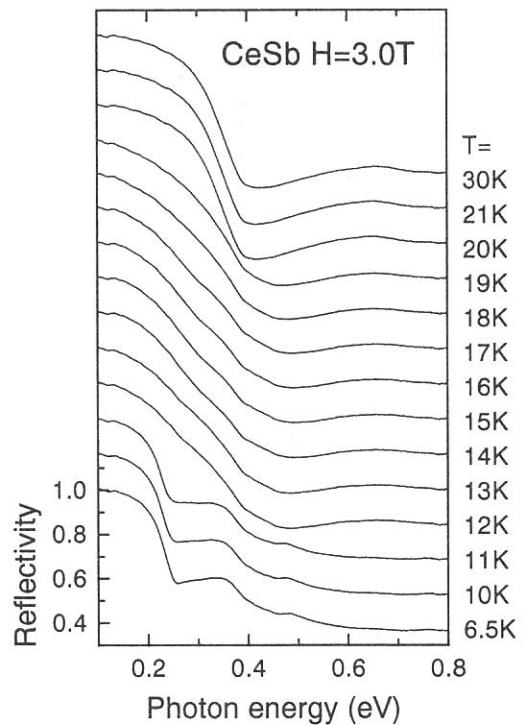The $\sigma_{xx}(\omega, T, H)$ spectra reflect the electronic

Fig. 1. Temperature dependence of the reflectivity spectrum of CeSb at 3.0 T as a function of the photon energy. Successive curves are offset by 0.2 for clarity.
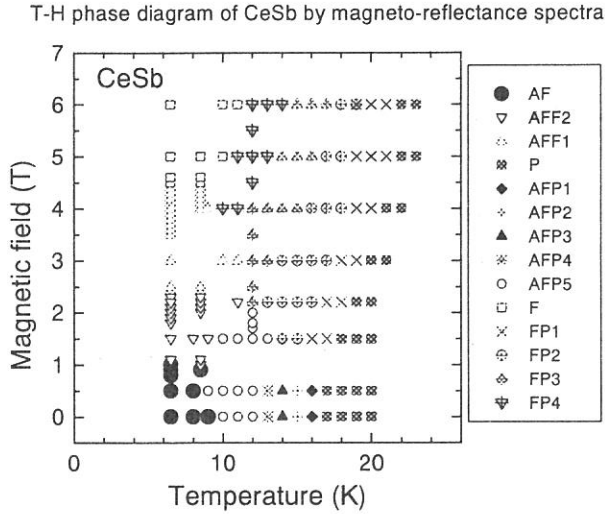
Fig. 2. Magnetic phase diagram determined by optical reflectivity measurement under magnetic field. The same marks indicate that the same spectrum has been obtained.

Fig. 3. (a) Optical conductivity spectra, σ'_{xx}, of the ferro-magnetic phase of CeSb at the temperature of 6.5 K and at the magnetic field of 6T (solid line) and that of para-magnetic phase at 20 K and at 0 T (dot line). (b) MCD optical conductivity spectra, $\sigma'_{\pm}$, of CeSb in the ferro-magnetic phase with the different selection rule of $\Delta m_j = \pm 1$, respectively.

structures in the magnetic phases. The optical conductivity observed in the energy range is due to the transition from the top of the valence band of Sb-$5p$ to the bottom of the conduction bad of the Ce-$5d$ bands according to the LaX band structure. Then, the change of the $\sigma_{xx}(\omega, T, H)$ spectra reflect the change of these bands.

The change of the electronic structure is considered to originate from not only the band folding due to the appearance of the long periodic structure of the ordered magnetic state but also the shifting of the energy band, because the change of the $\sigma_{xx}(\omega, T, H)$ spectrum cannot be explained only by the band folding.[5]

We measured the MCDR spectra in the ferro-magnetic phase for the detail analysis of the electronic structure. Figure 3 (a) is the $\sigma_{xx}(\omega, T, H)$ spectra with unpolarized light and figure 3 (b) the $\sigma_{\pm}(\omega, T, H)$ spectra with circularly polarized light of the ferro-magnetic phase. Here, $\sigma_{\pm}(\omega, T, H)$ indicates the different selection rule of the magnetic quantum number of $\Delta m_j = \pm 1$. From the figure, we can understand that the double peak at 0.4 eV belongs to the $\Delta m_j = +1$ and the shoulder structure at 0.65 eV to the $\Delta m_j = -1$.

The p band of the magnetic ordered state is explained by the p-f mixing theory by Takahashi and Kasuya.[6] According to the theory, one p band shifts to 0.5 eV above the Fermi level and the others remain at the same energy of the para-magnetic state. The energy is almost equal to that of the double peak structure. However the optical transition from the p valence band to the shifted p band is considered to be weak even if the Sb $5p$ - Ce $5d$ mixing is strong. While, the Ce $5d$ band should move close to the Fermi level in the ferro-magnetic phase. The electronic structure of the $5d$ band is considered to be the origin of the anomalous physical property and the complex magnetic phase diagram. However, the theoretical study has never done before. Further theoretical study is required.
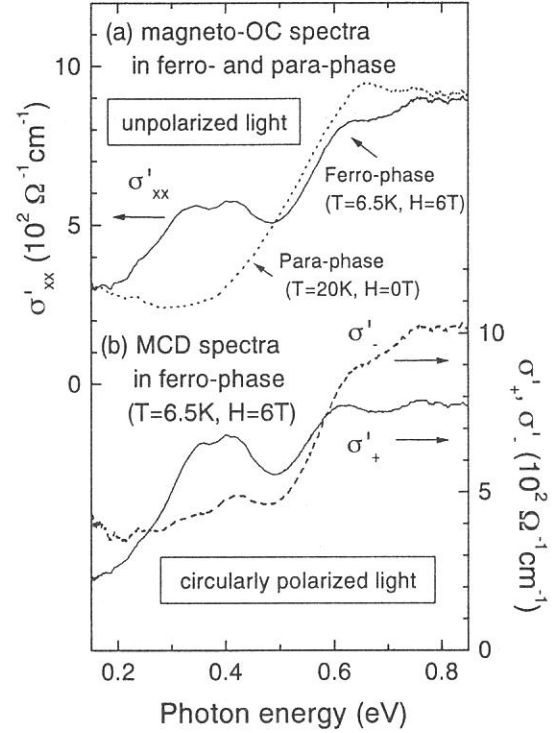
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Optical reflectivity study of the Kondo alloy system (Yb, Lu)B$_{12}$

H. Okamura, T. Inaoka, S. Kimura, T. Nanba,
F. Iga[A], S. Hiura[A], T. Takabatake[A], and J. Kleijn[A]

Department of Physics and Graduate School of Science and Technology,
Kobe University, Kobe 657-8501.
[A]Graduate School of Advanced Science of Matter,
Hiroshima University, Higashi-Hiroshima 739-8526

YbB$_{12}$ is one of the strongly correlated electron systems known as "Kondo semiconductors".[1] Upon cooling below ~ 80 K, an energy gap of 10-15 meV develops, and also the magnetic susceptibility shows a large decrease. These unique behaviors are believed to arise from strong interactions between the localized Yb 4f-electrons and free carriers, but the microscopic mechanism is not precisely known yet. Previously, we reported the detailed temperature-evolution of the energy gap in the optical conductivity spectrum of YbB$_{12}$.[2] We also found a characteristic absorption in the mid-infrared region. This peak, referred to as the "IR peak", is likely to arise from Yb 4f-related optical transitions, but its microscopic origin was unclear.

In the present work we study the optical spectra of the mixed system (Yb, Lu)B$_{12}$, in order to see how the energy gap and the IR peak is suppressed as the Yb ions are replaced with Lu ions. An Yb^{3+} has 13 electrons and 1 hole in the 4f shell, while a Lu^{3+} has 14 electrons filling up the 4f shell. Hence, the substitution of Lu for Yb results in a decrease in the magnetic moment due to Yb^{3+}. Figure 1 shows the optical conductivity spectra in the gap region of (Yb, Lu)B$_{12}$ at 8 K, normalized by those at 78 K. The clear energy gap seen for Yb 100 % sample is already much less clear for Yb 75 %, demonstrating a large effect of Yb replacement on the energy gap. It should be noted that the gap collapses by filing in from the bottom rather than becoming narrower, with the "shoulder" seen at ~40 meV nearly unshifted. Figure 2 shows the evolution of the IR peak for different Yb fractions. It is seen that, with decreasing Yb fraction, the IR peak red-shifts, becomes weaker and narrower, and finally merges into the Drude-like spectrum for the LuB$_{12}$. At lower temperatures (not shown here), the IR peak becomes narrower and slightly blue-shifts. Currently we are attempting to analyze these behaviors more quantitatively by fitting the spectra with Lorentz and Drude functions.

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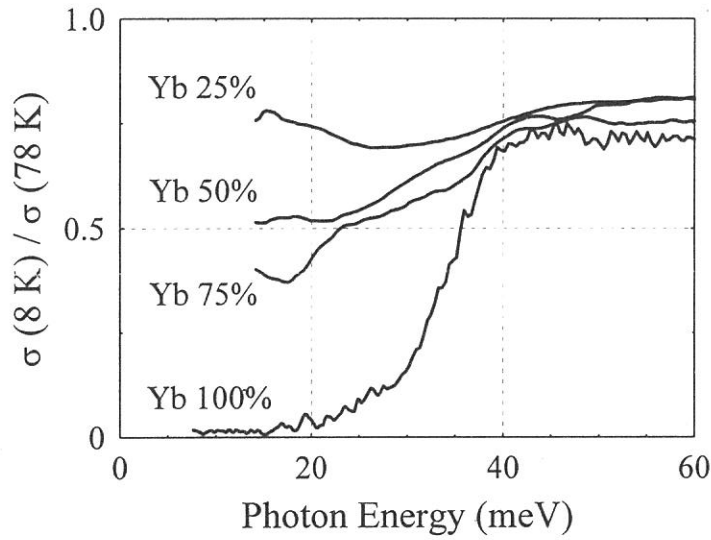
FIG. 1. Optical conductivity spectra of (Yb, Lu)B$_{12}$ in the gap region at T=8 K normalized by those at 78 K.
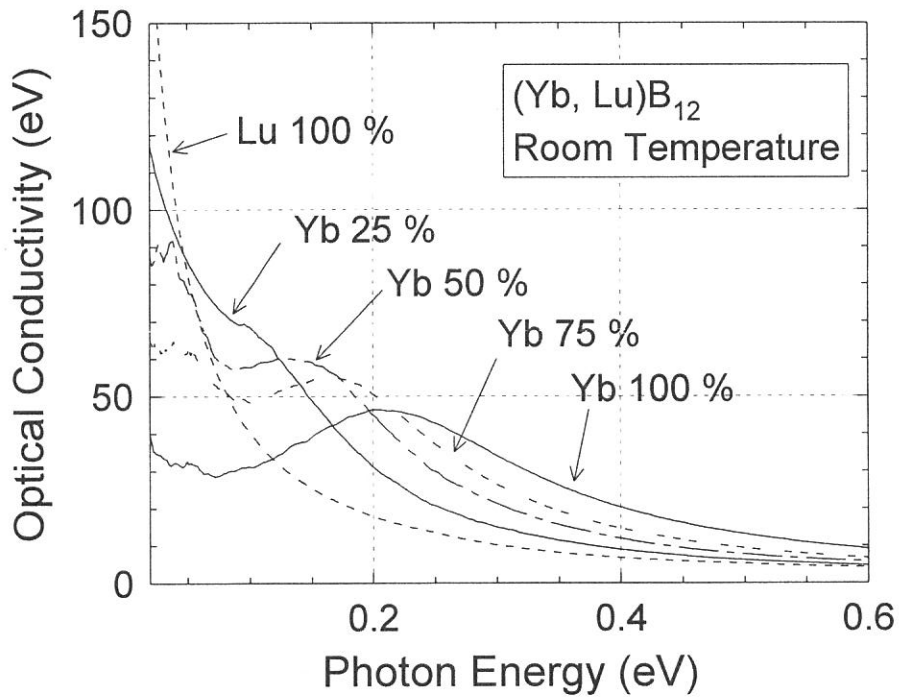
FIG.2 : Optical conductivity of (Yb, Lu)B$_{12}$ at room temperature for (Yb, Lu)B$_{12}$ with different Yb mole fractions.