Indirect and direct energy gaps in the Kondo semiconductor YbB$_{12}$.  

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Optical conductivity [$\sigma(\omega)$] of the Kondo semiconductor YbB$_{12}$ has been measured over wide ranges of temperature ($T=8-690$ K) and photon energy ($\hbar\omega \geq 1.3$ meV). The $\sigma(\omega)$ data reveal the entire crossover of YbB$_{12}$ from a metallic electronic structure at high $T$ into a semiconducting one at low $T$. Associated with the gap development in $\sigma(\omega)$, a clear onset is newly found at $\hbar\omega=15$ meV for $T \leq 20$ K. The onset energy is identified as the gap width of YbB$_{12}$ appearing in $\sigma(\omega)$. This gap in $\sigma(\omega)$ is interpreted as the indirect gap, which has been predicted in the band model of Kondo semiconductor. On the other hand, the strong mid-infrared (mIR) peak observed in $\sigma(\omega)$ is interpreted as arising from the direct gap. The absorption coefficient around the onset and the mIR peak indeed show characteristic energy dependences expected for indirect and direct optical transitions in conventional semiconductors.  

KEYWORDS: YbB$_{12}$, Kondo semiconductor, optical conductivity, indirect gap

YbB$_{12}$ has been well known$^{1-3}$ as an example of the Kondo semiconductors.$^{3-5}$ It develops a small energy gap at the Fermi level below 80 K.$^{1,2}$ The gap width in YbB$_{12}$ has been estimated to be 12.7 meV (136 K) from electrical resistivity,$^2$ 15 meV (180 K) from Hall effect,$^2$ and approximately 15 meV from electronic specific heat$^6$ and photoemission$^7$ experiments. The gap formation mechanism in the Kondo semiconductor has been discussed extensively.$^{3-5}$ In the so-called band model, the gap is regarded as a band gap resulting from the hybridization between a wide conduction (c) band and a flat f-electron band.$^{4,5}$ Here the gap width is renormalized to a much smaller value than those in conventional semiconductors, due to strong correlation of the f electrons. To calculate the temperature ($T$) dependence of the energy gap based on the band model, the periodic Anderson Hamiltonian$^8$ has been often used in conjunction with the dynamical mean field approximation.$^9-12$ Band calculations of YbB$_{12}$ including both the orbital degeneracy and the spin-orbit coupling have been also reported.$^{13,14}$ Recently, a theory of $T$-dependent energy gap in YbB$_{12}$ using realistic band structures has been reported.$^{15}$  

Previously, we reported an optical study of YbB$_{12}$ single crystals.$^{16}$ The optical conductivity spectrum, $\sigma(\omega)$, of YbB$_{12}$ clearly showed an energy gap formation below 80 K. The gap development involved a progressive depletion of $\sigma(\omega)$ below a shoulder at $\sim 40$ meV. In addition, we observed a strong mid-infrared (mIR) absorption in $\sigma(\omega)$ peaked at $\sim 0.25$ eV, which was also strongly $T$-dependent. The evolution of $\sigma(\omega)$ in the diluted system Yb$_{1-x}$Lu$_x$B$_{12}$ was also studied in detail.$^{17}$  

This Letter reports $\sigma(\omega)$ data measured on YbB$_{12}$ single crystals having a higher quality than the previous ones.$^{16}$ They show a residual resistivity ratio exceeding 10$^5$ and no impurity-related Curie tail in the low-$T$ magnetic susceptibility.$^6$ In addition, the temperature and photon energy ranges of the experiment have been extended, from $T=20-290$ K and $\hbar\omega \geq 7$ meV in the previous work$^{16}$ to $T=8-690$ K and $\hbar\omega \geq 1.3$ meV in this work. The obtained $\sigma(\omega)$ reveals the entire evolution of electronic structures from metallic to semiconducting ones with decreasing $T$. Below 20 K, $\sigma(\omega)$ has revealed a clear onset at 15 meV, which we identify as the energy gap width. The energy of 15 meV agrees well with the gap widths obtained by other experimental techniques.$^{2,3,6,7}$ We conclude that the observed energy gap of 15 meV in $\sigma(\omega)$ arises from an indirect gap, predicted by the band model of the Kondo semiconductor. The mIR peak, on the other hand, is interpreted as arising from the direct gap. These assignments are supported by the analysis of absorption coefficient.  

The single crystal of YbB$_{12}$ (batch number #71) was grown as previously described.$^2$ A disk-shaped sample of 4.5 mm diameter was cut from the crystal, and mechanically polished for optical measurements. The reflectivity spectrum, $R(\omega)$, of the sample was measured at the above-mentioned ranges of $T$ and $\omega$.$^{18}$ $\sigma(\omega)$ spectra were obtained from the Kramers-Kronig (K-K) analysis$^{19}$ of the measured $R(\omega)$ spectra, which were extrapolated using the Hagen-Rubens function$^{19}$ below the measured energy range. Other details of the optical experiments for $\hbar\omega \geq 4$ meV were similar to those previously described.$^{16,17}$ $R(\omega)$ between 1.3 and 4 meV (10-30 cm$^{-1}$) were measured using a THz synchrotron radiation source at the beam line BL6B of UVSOR.$^{20}$ Institute for Molec- 

ular Science. The sample was cooled by a continuous-flow liquid He cryostat. A rapid-scan, Martin-Pupplet-type interferometer was used with an InSb bolometer to record $R(\omega)$.  

Figures 1(a) and 1(b) show the measured $T$ dependences of $R(\omega)$ and $\sigma(\omega)$ in the infrared region. (Higher-energy spectra were reported previously.$^{16}$) With decreasing $T$ from 295 K, the broad dip centered near
0.15 eV in \( R(\omega) \) becomes deeper, and \( R(\omega) \) below 40 meV is strongly reduced at \( T \leq 80 \) K. These two features in \( R(\omega) \) give rise to the mIR peak in \( \sigma(\omega) \) centered at 0.2-0.25 eV and the energy gap formation in \( \sigma(\omega) \) below 40 meV. These overall features are very similar to those previously reported. With increasing \( T \) above 295 K, the mIR peak in \( \sigma(\omega) \) becomes progressively weaker. At 690 K, the overall \( \sigma(\omega) \) is similar to that of a metal, i.e., \( \sigma(\omega) \) is basically a decreasing function of energy. Namely, the entire crossover from metallic to semiconducting (insulating) electronic structures in YbB\(_{12}\) has been revealed in the present \( \sigma(\omega) \) data.

The detailed \( T \)-evolutions of \( R(\omega) \) and \( \sigma(\omega) \) due to the gap formation are shown in Figs. 1(c) and 1(d), respectively. As in the previous result,\(^{16}\) the gap formation in \( \sigma(\omega) \) starts around 80 K, with a shoulder appearing at \( \sim 40 \) meV (indicated by the black arrow). As the gap develops with decreasing \( T \), the density of free carriers decreases progressively.\(^2\) This results in, as seen in Figs. 1(c) and (d), the shifts of the plasma edge (sharp minimum) in \( R(\omega) \) and the decrease of the Drude-like component (the rise toward \( \omega=0 \)) in \( \sigma(\omega) \). At 20 and 8 K, \( \sigma(\omega) \) has a clear onset at 15 meV (indicated by the red arrow), below which the spectral weight is very small. The onset in \( \sigma(\omega) \) results from the hump in \( R(\omega) \) located around 15 meV (indicated by the blue arrow). This hump in \( R(\omega) \), which had not been observed previously,\(^{16}\) has been reproduced in repeated experiments. Although \( R(\omega) \) at 8 K does not approach 1 even near \( \omega=0 \), a Hagen-Rubens extrapolation has been used similarly to other data at higher \( T \)’s, since a small density of free carriers are still present even at 8 K.\(^{2,6,21}\) We have found, however, that the onset of \( \sigma(\omega) \) at 15 meV is unaffected by details of the extrapolation used. Hence, the onset is neither due to an experimental error nor due to an artifact of the K-K analysis, but it should be an intrinsic feature. We conclude that the energy gap width of YbB\(_{12}\) observed in \( \sigma(\omega) \) is 15 meV, as given by the onset energy. We had previously overestimated the gap width to be 25 meV, due to the lack of a clear onset in the previous \( \sigma(\omega) \) data.\(^{16}\) Compared with the above-mentioned gap widths \( (E_g) \) in the total density of states (DOS) obtained by other experimental techniques,\(^7,2,7\) it is clear that the gap width in \( \sigma(\omega) \) is just equal to \( E_g \). It is interesting that a magnetic excitation peak has also been observed at \( \sim 15 \) meV in the inelastic neutron scattering of YbB\(_{12}\).\(^{22,23}\)

According to the band model of Kondo semiconductor, as sketched in Fig. 2, the \( c-f \) hybridization state involves both an indirect gap and a direct gap.\(^4,5\) The indirect gap corresponds to \( E_g \), which can be measured by various experiments as already mentioned. Hence, in the band model of YbB\(_{12}\), the present result indicates that the energy gap appearing in \( \sigma(\omega) \) is the indirect gap. In fact, the band calculation has shown that the minimum energy gap in YbB\(_{12}\) should be an indirect gap.\(^13\) Note that, however, such indirect optical transitions are forbidden by the momentum conservation rule within the first-order optical processes, which involve the absorption of a photon only.\(^{19,24}\) This point will be discussed later.

We had previously conjectured\(^{16}\) that the gap in \( \sigma(\omega) \) corresponded to the direct gap and the mIR peak to some interband transition due to the band structure of YbB\(_{12}\). Since then, however, YbAl\(_3\), a typical mixed-valent metal, has also shown a mIR peak\(^{25}\) very similar to that for YbB\(_{12}\). In addition, many other Yb-based metals, including YbInCu\(_4\),\(^{26}\) YbRh\(_2\)Si\(_2\), YbAl\(_3\), YbCu\(_2\)Si\(_2\), YbNi\(_2\)Ge\(_2\) and YbCuAl\(_2\),\(^{28}\) have also shown a similar mIR peak. Namely, the mIR peak is a universal feature for these Yb-based compounds, and it is likely to result from a common electronic structure shared by these compounds. Within the band model of a mixed-valent or a heavy-fermion metal,\(^8\) the underlying electronic structure is exactly analogous to that for the Kondo semiconductor sketched in Fig. 2. Hence, these results strongly suggest that the mIR peak is due to the optical transitions across the direct gap in the band model, as sketched in Fig. 2.

We have interpreted the onset of \( \sigma(\omega) \) at 15 meV as the absorption edge at the indirect gap and the mIR peak as arising from the direct gap within the band model. As already mentioned, indirect optical transitions are forbidden within the first-order optical processes. However, they are allowed within the second-order processes involving the absorption/emission of a photon \( \text{and a phonon} \), the latter of which provides the required momentum transfer.\(^{24}\) In such an indirect transition, a photon is either emitted or absorbed by the electron, followed by or preceded by a virtual electronic transition to or from an intermediate state. The process with a phonon absorption can occur only at sufficiently high \( T \), but that with a phonon emission may occur even at low \( T \). It is well known that indirect-gap semiconductors actually show phonon-assisted indirect absorption even at low \( T \).\(^{24}\) A good example is Ge,\(^{29}\) which is a band semiconductor with the indirect gap \( (E_{\text{ind}}) \) of \( \sim 0.74 \) eV and the minimum direct gap \( (E_{\text{dir}}) \) of \( \sim 0.89 \) eV at 4.2 K. At 4.2 K, Ge shows quite sizable absorption at photon energies well below \( E_{\text{dir}} \).\(^{29}\) The photon-energy dependence of the optical absorption coefficient\(^{30} \) near the direct and indirect absorption edges can be calculated assuming parabolic band edges: \( \alpha^2 \) is linear in energy near the direct one and \( \alpha^4 \) is linear in energy near the indirect one, where the energy is measured from \( E_{\text{dir}} \) and \( E_{\text{ind}} \), respectively.\(^{24}\) Such dependences have been actually observed for conventional semiconductors.\(^{24,29}\) For comparison, \( \alpha^2 \) and \( \alpha^4 \) of YbB\(_{12}\), obtained from the K-K analysis of \( R(\omega) \), are plotted in Fig. 3 together with \( \sigma(\omega) \). \( \alpha^2 \) is apparently linear in energy over a width of \( \sim 0.06 \) eV, which coincides with the range where the mIR peak is centered in \( \sigma(\omega) \). \( \alpha^4 \) is also linear in energy above the onset at 15 meV. Hence, the present optical data possess the well-known characteristics of indirect and direct absorptions for conventional semiconductors. The intercept of the linear portion (the broken line in Fig. 3) with the energy axis gives the gap width.\(^{24}\) Hence the direct gap in YbB\(_{12}\) is estimated to be \( \sim 0.18 \) eV in this analysis.

As mentioned above, the characteristic energy dependence of \( \alpha \) for indirect and direct transitions have been derived for simple parabolic bands.\(^{24}\) The actual band...
dispersions in YbB_{12} should be far more complicated, as actually shown by the band calculations.\textsuperscript{13,14} In addition, it is even unclear whether phonon-assisted indirect transitions are indeed possible in YbB_{12}, since such a process has not been examined with the phonon dispersion of YbB_{12} taken into account. Therefore, it is rather surprising that the measured $\alpha$ of YbB_{12} closely follows the characteristic energy dependence predicted by the simplified model.

Theoretical calculations of $T$-dependent $\sigma(\omega)$ for the Kondo semiconductor have been made using the periodic Anderson Hamiltonian with the dynamical mean field approximation.\textsuperscript{9-12} Earlier works\textsuperscript{9-11} assumed first order optical processes, hence the calculated $\sigma(\omega)$ contained the direct gap only. Accordingly, the calculated $\sigma(\omega)$ at low $T$ showed an extremely sharp onset at $E_{\text{dir}}$. Hence, to compare the calculated $\sigma(\omega)$ with the experimental $\sigma(\omega)$, some broadening would have to be introduced into the former. Recently, it has been suggested\textsuperscript{12} that many-body scattering, inherent in strongly corre-

dated $f$-electron system, may provide the momentum transfer needed for indirect transitions. The calculated $\sigma(\omega)$ in this model\textsuperscript{12} showed a long tail below $E_{\text{dir}}$, showing better agreement with the experimental $\sigma(\omega)$. Note that such a process is analogous to the phonon-assisted $(\omega)$, some broadening would have to be introduced into the former. Recently, it has been suggested\textsuperscript{12} that many-body scattering, inherent in strongly corre-

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In conclusion, the present $\sigma(\omega)$ data reveal the entire crossover of YbB_{12} from metallic to semiconducting electronic structures. At low $T$, a clear onset of $\sigma(\omega)$ is observed at 15 meV, and this energy is identified as the gap width in $\sigma(\omega)$. This value agrees very well with $E_g$ in the total DOS obtained by other experiments. The observed gap in $\sigma(\omega)$ is interpreted as the indirect gap within the hybridization-band model of the Kondo semiconductor. The energy dependence of the absorption coefficient around the onset and the mIR peak are indeed found to follow the characteristic patterns of indirect and direct absorptions, respectively, known for conventional band semiconductors. It is suggested that phonon-assisted indirect transitions may be important for a better understanding of $\sigma(\omega)$ for YbB_{12}.

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agitation. \( \alpha(\omega) = (2\pi\omega/c)k(\omega) \), where \( c \) is the speed of light and \( k(\omega) \) is the imaginary part of the complex refractive index, hence \( \alpha(\omega) \) can be calculated from the K-K analysis of \( R(\omega) \).\(^{19,24}\)

Fig. 1. (Color) (a) Optical reflectivity \( R(\omega) \) and (b) conductivity \( \sigma(\omega) \) of YbB\(_2\) between 8 and 690 K. The weak dip in \( R(\omega) \) around 0.4 eV at 8 K is due to the absorption by ice formed on the sample, which has negligible effect on \( \sigma(\omega) \) in (b). (c) and (d) show \( R(\omega) \) and \( \sigma(\omega) \), respectively, below 120 K in the low-energy region. The blue arrow in (c) indicates the hump in \( R(\omega) \), and the black and red arrows in (d) indicate, respectively, the shoulder and the onset in \( \sigma(\omega) \). The broken curves are the extrapolations (see text).

Fig. 2. Sketch of the band model for the Kondo semiconductor.\(^4,5\) The hybridization between an otherwise flat \( f \) band and a wide conduction band results in the direct gap and the indirect gap \( (E_g) \). The arrows indicate the relevant optical transitions.

Fig. 3. (a) Optical conductivity \( \sigma \), (b) absorption coefficient \( \alpha \), (c) \( \alpha^2 \), and (d) \( \alpha^{\beta} \) of YbB\(_2\) at 8 K as a function of photon energy. The broken lines are guide to the eye, indicating the linear dependence on photon energy discussed in the text.
FIG. 1
Okamura et al.
FIG.2
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FIG. 3
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