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(Citation)
Physical Review B,62(20):R13265-R13269

(Issue Date)
2000-11

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90000410

PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 62, NUMBER 20 15 NOVEMBER 2000-II

RAPID COMMUNICATIONS

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Optical conductivity of $Yb_{1-x}Lu_xB_{12}$: Energy gap and mid-infrared peak in diluted Kondo semiconductors

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(Received 7 August 2000)

We have measured the optical conductivity $\sigma(\omega)$ of $Yb_{1-x}Lu_xB_{12}$ ($0 \leqslant x \leqslant 1$), where the system evolves from a Kondo semiconductor at $x=0$ to a nonmagnetic metal at $x=1$. For $x=0$, $\sigma(\omega)$ exhibits a clear energy gap with an onset at ~ 20 meV and a shoulder at 38 meV. As x increases, the gap is rapidly filled in from the bottom, while the shoulder remains at ~ 40 meV up to $x=\frac{1}{2}$. These results suggest that Lu substitution into YbB_{12} produces an in-gap band, but the characteristic energy for the gap remains unchanged in a wide range of x. Spectral evolutions of a characteristic mid-infrared peak, which results from Yb $4f$-derived states near the Fermi level, suggest a strong coupling of Yb $4f$ electrons with conduction electrons.

Physics of gap-forming Kondo lattice compounds, often referred to as the ''Kondo semiconductors'' (or equivalently Kondo insulators), has been a target of active research for a few decades.[1,2] They are characterized by the opening of a small energy gap (of the order of 10 meV) at low temperatures, associated with a large decrease of magnetic susceptibility. Among the known Kondo semiconductors, YbB_{12} has been the only Yb-based compound so far.[3] After the successful growth of high-quality single crystals by Iga *et al.*,[4] physical properties of YbB_{12} have gained renewed interest, with various experiments performed on single-crystalline samples. They include optical,[5] tunneling,[6] photoemission,[7] and neutron-scattering[8] spectroscopies. The optical conductivity spectrum, $\sigma(\omega)$, of YbB_{12} has shown an energy gap of ~ 20 meV upon cooling below 80 K, and also a characteristic mid-infrared peak due to the Yb $4f$-derived states near the Fermi level (E_F).[5] More recently, magnetic, transport and thermal properties of $Yb_{1-x}Lu_xB_{12}$ have been studied.[9,10] Substituting nonmagnetic Lu^{3+} for Yb^{3+} lowers the electronic coherence among the Yb $4f$ orbitals at different sites, without substantially affecting the electronic structures other than $4f$-related states. (The difference in lattice constant between YbB_{12} and LuB_{12} is only 0.07 %.[3]) Hence, this ''diluted'' Kondo semiconductor system may give important information about the Kondo semiconducting gap.

In this work we study $\sigma(\omega)$ spectra of $Yb_{1-x}Lu_xB_{12}$ ($0 \leqslant x \leqslant 1$) in order to examine the evolutions of energy gap and low-energy excitations with varying Yb/Lu concentration. We observe, with increasing x, that the energy gap in $\sigma(\omega)$ is suppressed by filling in from the bottom, rather than by narrowing. Our results give strong evidence that an in-gap band grows with increasing x, and that the characteristic energy for the gap, given by the shoulder, is unchanged over a wide range of x. The mid-infrared peak due to Yb $4f$ states shows both a redshift and a narrowing with increasing x. These spectral evolutions are discussed in terms of the coupling between the conduction and the $4f$ electrons.

The $Yb_{1-x}Lu_xB_{12}$ single crystals ($x=0, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, \frac{7}{8}, 1$) were grown by the floating-zone method using an image furnace equipped with four Xe lamps.[4] Specimens of approxi-

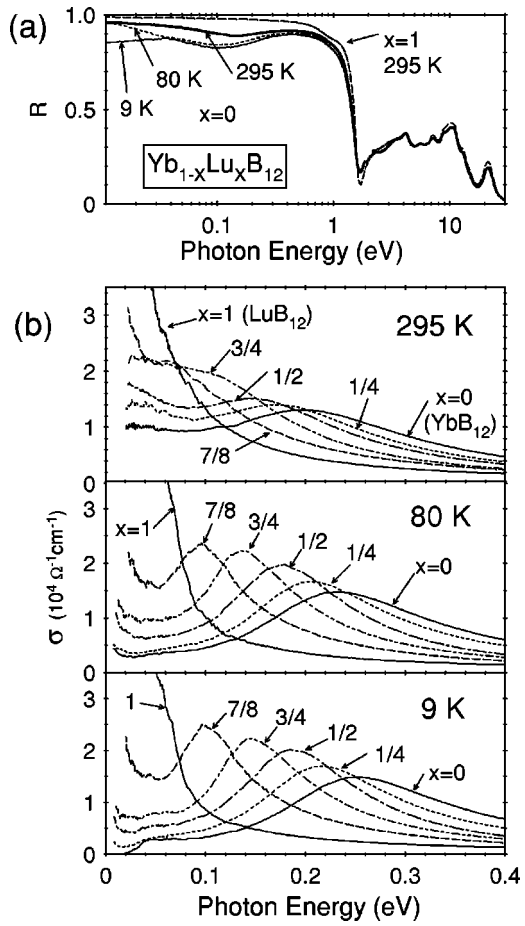

FIG. 1. Optical reflectivity (R) and conductivity (σ) spectra of $Yb_{1-x}Lu_xB_{12}$. (a) R of $x=1$ (LuB_{12}) at 295 K and those of $x=0$ (YbB_{12}) at 295, 80, and 9 K. (b) σ for various values of x at 295, 80, and 9 K.

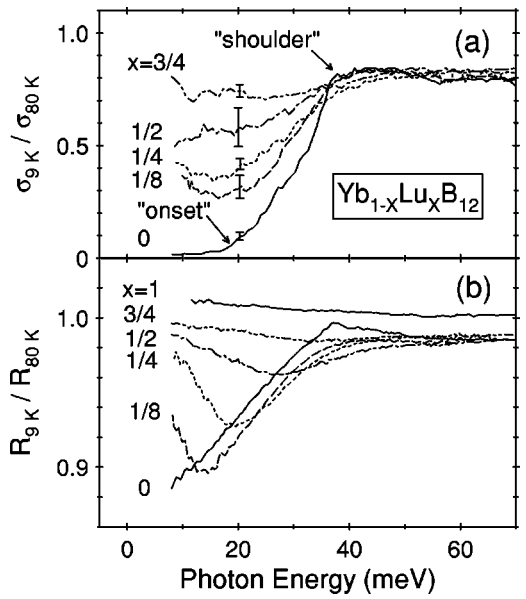

FIG. 2. (a) Optical conductivity (σ) and (b) reflectivity (R) of $Yb_{1-x}Lu_xB_{12}$ at 9 K normalized by those at 80 K. The error bars are derived from the uncertainty in the measured R (Ref. 12).

mately 5 mm diameter were cut from the ingots, and mechanically polished. $\sigma(\omega)$ spectra were obtained from the measured optical reflectivity spectra $[R(\omega)]$ of $Yb_{1-x}Lu_xB_{12}$ using the Kramers-Kronig relations.[11] The optical reflectivity experiments were performed under a near-normal incidence configuration, using a Fourier interferometer (Bruker IFS 66v) and conventional sources for photon energies 7 meV $\leqslant \hbar\omega \leqslant$ 2.5 eV.[12] For the higher-energy region, the $R(\omega)$ spectra of YbB_{12} and LuB_{12} measured with a synchrotron radiation source up to 50 eV (Ref. 5) were used. Extrapolations of the form $R(\omega) \propto 1-a\sqrt{\omega}$ were used to complete the spectra in the lower-energy end, and $R(\omega) \propto \omega^{-4}$ in the higher-energy end.[11]

Figure 1(a) shows $R(\omega)$ of LuB_{12} at 295 K, and those of YbB_{12} at 295, 80, and 9 K. Figure 1(b) shows $\sigma(\omega)$ of $Yb_{1-x}Lu_xB_{12}$ below 0.4 eV at 295, 80, and 9 K. The $R(\omega)$ spectra have a clear plasma cutoff (ω_p) near 1.2 eV, and sharp structures above 4 eV due to interband transitions.[13] Below ω_p, LuB_{12} ($x=1$) has a sharp rise in $\sigma(\omega)$, which is typical of a good metal. For $x<1$, in contrast, $\sigma(\omega)$ has a broad, strong peak in the mid-infrared, which we refer to as the IR peak.[5] The IR peak is gradually shifted toward lower energy with increasing x, and toward higher energy with decreasing temperature (T). Another important feature in $\sigma(\omega)$ is the depletion of $\sigma(\omega)$ below 40 meV seen at 9 K, i.e., an energy gap formation. The detailed T dependence of the energy gap for YbB_{12} ($x=0$) has been already reported.[5] Below we first analyze the energy gap evolution with varying x.

To show the energy gap evolutions more clearly, in Fig. 2(a) we plot the $\sigma(\omega)$ spectra at 9 K normalized by those at 80 K. For comparison, in Fig. 2(b) we also plot the normalized $R(\omega)$ spectra. For $x=0$, the gap formation is evident as a strong depletion of $\sigma(\omega)$ and $R(\omega)$ below $\sim$38 meV. $\sigma(\omega)$ at 9 K has an onset at $\sim$18 meV, above which it rises quickly to a shoulder, as indicated in Fig. 2(a). As x increases, the gap in $\sigma(\omega)$ is progressively suppressed by filling in from the bottom, rather than by narrowing. The strong influence of the Lu substitution is evident at $x=\frac{1}{8}$, where $\sigma(\omega)$ already has a large in-gap spectral weight, and the gap is now a ''pseudogap.'' Another remarkable feature in the $\sigma(\omega)$ spectra is that a shoulder is observed at $\sim$40 meV for $0 \leqslant x \leqslant \frac{1}{2}$, as indicated in Fig. 2(a). Although the shoulder for $x \geqslant \frac{1}{8}$ is not as clear as that for $x=0$, apparently it stays at about the same energy. This means that the energy range of spectral depletion in $\sigma(\omega)$ is almost unchanged for $x \leqslant \frac{1}{2}$, although the depletion becomes weaker as x increases.

The transport experiments[3,9] on $Yb_{1-x}Lu_xB_{12}$ have shown that the electrical resistivity (ρ) of YbB_{12} at low T is strongly reduced by substituting a small amount of Lu for Yb. This result is consistent with the present observation of the rapid filling of gap in $\sigma(\omega)$ at small x. These results indicate that the density of states (DOS) at E_F increases strongly with a small amount of Lu substitution. In addition, $\rho(T)$ shows thermally activated T dependence only for $x \leqslant \frac{1}{2}$, which indicates the absence of a transport gap in dilute Yb regime ($x > \frac{1}{2}$).[3,9] In contrast, the present $\sigma(\omega)$ data show that the DOS at E_F is slightly reduced even at $x=\frac{3}{4}$, as evidenced by the small depletion of spectral weight below $\sim$50 meV. In terms of magnetic properties of the Kondo semiconductors, an important energy scale is given by T_{max}, the temperature at which a maximum is observed in $\chi(T)$,

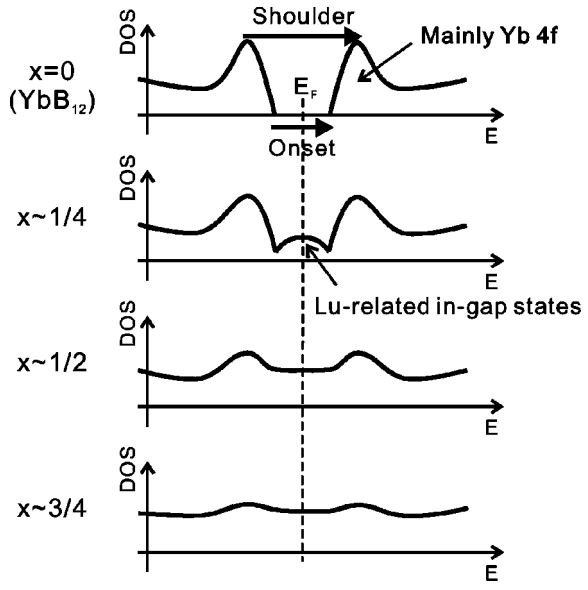

FIG. 3. Schematic illustrations for the evolution of density of states (DOS) in $Yb_{1-x}Lu_xB_{12}$ suggested from the present results.

the T dependence of the magnetic susceptibility.[1,2] At a higher T regime, $\chi(T)$ shows a Curie-Weiss (local moment) behavior, but below T_{max} it shows a rapid decrease, hence T_{max} marks a crossover between the two characteristic regimes. From the magnetization experiments on single crystalline $Yb_{1-x}Lu_xB_{12}$, T_{max} is about 80 K for YbB_{12}, and this value remains almost the same for $0 \leqslant x \leqslant 1/2$.[17] This behavior is quite similar to the present result that the shoulder in $\sigma(\omega)$ remains unshifted for $x \leqslant \frac{1}{2}$. This is remarkable since the observed characteristic energies in optical and magnetic properties both show the same behavior, strongly suggesting that they share a common origin.

Theoretical models for the Kondo semiconductors include the periodic Anderson model[14–16] and its strong-correlation limit, the Kondo lattice model.[18,19] In the former, the Kondo semiconducting gap is realized as a hybridization gap between a broad conduction band and a narrow f band, where the gap is strongly renormalized by the strong on-site Coulomb interaction. The model has been used to study the effects of nonmagnetic impurities in Kondo semiconductors.[15,16] It has been predicted that the $4f$ holes created by the substituted nonmagnetic ions give rise to an ''impurity band'' within the gap, without substantially narrowing the original gap.[15] As the concentration of the substituted ions becomes larger, the band grows, finally filling up the gap.[16] The observed evolution of the energy gap in $\sigma(\omega)$ for $Yb_{1-x}Lu_xB_{12}$ appears consistent with these predictions. Namely, the observed filling of the gap in $\sigma(\omega)$ with increasing x can be understood as the growth of an in-gap band. Also, the observation that the shoulder is unshifted over a wide range of x is consistent with the filling of a gap rather than the narrowing. The suggested evolution of the energy gap is illustrated in Fig. 3.

The rapid filling of the gap in $\sigma(\omega)$ at small x clearly shows the importance of lattice effects in producing a well-developed gap. On the other hand, the shoulder position (E^*) is almost unchanged over a wide range of x, which strongly implies that E^* is closely related with some *single-site* energy scale of Yb^{3+} in YbB_{12}. Considering the Kondo

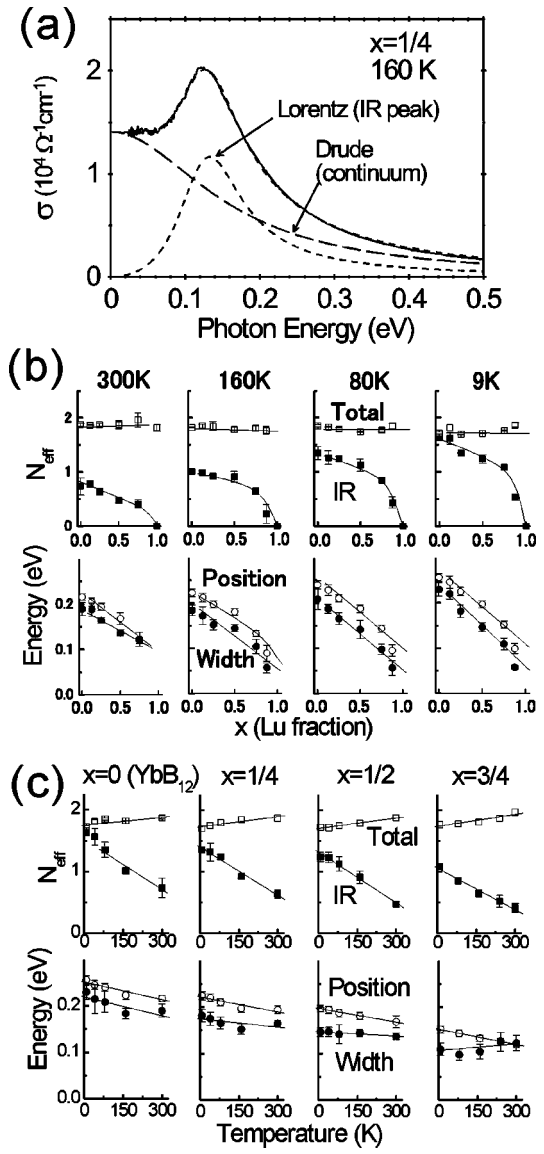

FIG. 4. Fitting results of the IR peak in the optical conductivity (σ) of $Yb_{1-x}Lu_xB_{12}$. (a) An example of the fitting for $x=\frac{1}{4}$. The solid line shows the measured spectrum, and dotted and dashed lines show the fitting. (b) The effective carrier density per formula unit (N_{eff}) for the total (Drude + Lorentz) intensity and that for the IR (Lorentz) peak, and the position and the width of IR peak are plotted as a function of x at four temperatures. (c) The same data as in (b), but plotted as a function of temperature for four values of x. In (b) and (c), the solid lines are guide to the eye, and the error bars are derived from the uncertainty in the measured R (Ref. 12).

semiconducting properties of YbB_{12}, a most likely single-site energy scale here is the exchange (Kondo) coupling between the conduction (c) electrons and the Yb^{3+} $4f$ electrons. For a localized spin in a metal, the characteristic energy for such a coupling is given by T_K, the impurity Kondo temperature. In a gap-forming Kondo lattice like YbB_{12}, however, it is not apparent whether the impurity T_K correctly gives this coupling energy at low T,[20] and whether E^* can be directly related to T_K. Nevertheless, the observed evolution of the energy gap with varying x strongly suggests that the c-f coupling determines E^*, i.e., the energy range over which a spectral depletion occurs in $\sigma(\omega)$. On the other

hand, lattice effects are important, as stated earlier, to produce a stronger depletion of spectral weight for $\hbar\omega \leqslant E^*$.

Based on the comparison of $\sigma(\omega)$ between YbB_{12} and LuB_{12}, it was conjectured[5] that the IR peak resulted from optical transitions between Yb $4f$-related states near E_F and a broad conduction band (derived mainly from Yb $5d$ and B $2p$). To perform quantitative analyses, we have fitted the spectral shape of the IR peak for $Yb_{1-x}Lu_xB_{12}$ using the classical Lorentz oscillator model, and the broad continuum toward $\omega=0$ using the Drude model.[11] An example of the fitting[21] for $x=\frac{1}{4}$ is shown in Fig. 4(a). Using the optical sum rule,[11] the effective carrier density N_{eff} contributing to $\sigma(\omega)$ below $\omega=\omega_p$ can be obtained as

$$N_{eff}=\frac{n}{m^*}=\frac{2m_0}{\pi e^2}\int_0^{\omega_p}\sigma(\omega)d\omega. \qquad (1)$$

Here, n is the carrier density, m^* is the effective mass in units of the rest electron mass, m_0. In Figs. 4(b) and 4(c), N_{eff} for the total $\sigma(\omega)$ (the sum of fitted Drude and Lorentz contributions) and that for the IR peak (fitted Lorentz) are plotted as functions of x and T, together with the position and the width of the IR peak. Figure 4(b) shows that N_{eff} contributing to the IR peak is strongly nonlinear in $1-x$, and hence does not scale with the number of Yb $4f$ electrons. (Note that the valence of Yb ions in $Yb_{1-x}Lu_xB_{12}$ is almost independent of x.[3]) The peak energy and the width of the IR peak show large, linear decreases with increasing x, which should be closely related to the evolution of Yb $4f$ states near E_F.[22] Then the decrease in peak energy may indicate that *the position of Yb $4f$-derived states becomes closer to E_F with decreasing Yb density*. In addition, the decrease in the width indicates that *the Yb $4f$-derived band near E_F becomes narrower for lower Yb concentration*. This is reasonable since lowering the Yb density reduces the intersite coupling (or the coherence as stated below), leading to a narrower band. Figure 4(c) shows that N_{eff} for the IR peak increases markedly with decreasing T at all x. Note that *decreasing T* and *increasing* Yb density have *qualitatively similar effects on the IR peak*: both increase the intensity and the peak energy, although the density effects are quantitatively much greater. In a dense Kondo system, with decreasing T or with increasing density of Kondo ions, more coherence develops among the local ''Kondo singlets'' formed by f and c electrons at different sites. Hence the similar T and x dependences of the IR peak are likely to result from varying degree of coherence as functions of x and T. Note that the Drude component also has large x and T dependence, and that the combined intensity (Drude + IR peak) is kept almost constant, $N_{eff}\sim 1.8$, with varying x and T. Namely, a *spectral weight transfer* exists between the Drude component and the IR peak, which demonstrates that *the dynamics of the conduction electrons and the Yb $4f$ electrons are strongly connected to each other*. This is consistent with the concept of coherence mediated by the c-f coupling, which is highly sensitive to changes in T and the density of Kondo ions. In fact, the T-induced spectral changes of the IR peak are remarkably large[23] in the entire range of x, even at high temperatures where $\sigma(\omega)$ has no energy gap.

In conclusion, we have studied the evolution of energy gap and characteristic infrared absorption in $\sigma(\omega)$ of $Yb_{1-x}Lu_xB_{12}$. The energy gap of ~ 20 meV at $x=0$ is rapidly filled in with increasing x, while the shoulder at ~ 40 meV remains unshifted in a wide range of x, $0 \leqslant x \leqslant \frac{1}{2}$. These results show that the energy range of spectral depletion is determined by a single-site property of Yb^{3+}, very likely to be the coupling of Yb $4f$ spin and conduction electrons, and that the degree of spectral depletion below the shoulder is determined by lattice effects. The infrared absorption, originating from the Yb $4f$ states near E_F, is also found highly sensitive to changes in x and T. We have suggested this to be a consequence of strong coupling between Yb $4f$ and c electrons and that among $4f$ electrons at different Yb sites, which are sensitive to changes in T and x.

We would like to thank T. Mutou for many stimulating discussions on various theoretical aspects of the Kondo semiconductor. We acknowledge financial support from the REIMEI Rsearch Resources, the Atomic Energy Research Institute, the Electric Technology Research Foundation of Chugoku, and the Grants-in-Aid from the Ministry of Education, Science, and Culture.

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[12] The accuracy (reproducibility) of the measured R in the far-infrared at 295 K and below 80 K were within $\pm 0.5\%$ and $\pm 1\%$, respectively, and that in the relative changes of R at different T below 80 K [see Fig. 2(b)] was within $\pm 0.3\%$. The accuracy of R in the mid-infrared was better than those in the far infrared.

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[20] For a $4f^1$ or a $4f^{13}$ *impurity in a metal*, T_K and T_{max} have a universal relation $T_K \simeq 3T_{max}$ [N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. Lett. **54**, 230 (1985)]. This relation has been often applied to Kondo semiconductors as well, but without justification. For Kondo semiconductors, although T_{max} is certainly an important energy scale as discussed in the text, it is unclear whether the T_K given as above is also physically meaningful at low T where the gap opens.

[21] When a (pseudo)gap is present at low T, we used an additional Lorentz oscillator function to fit the shoulder.

[22] Lu $4f$-derived states do not contribute to the IR peak since they are located several eV below E_F.

[23] The T range of 9–295 K is much lower in energy than the IR peak energies, 0.15–0.25 eV corresponding to 1700–2800 K. Hence the observed spectral changes of IR peak with T appear much greater than that expected from thermal broadening effects only.