Physical Properties of Actinde and Rare Earth Compounds
JJAP Series 8 (1993), pp. 100–103

# Optical Conductivity of Rare-Earth Hexaborides

Takao NANBA, Shin-ichi KIMURA[1], Mitsuhiro MOTOKAWA,
Satoru KUNII[2] and Tadao KASUYA[2]

*Faculty of Science, Kobe University, Nada-ku, Kobe 657*
[1]*Research Institute for Scientific Measurements, Tohoku University, Aoba-ku, Sendai 980*
[2]*Faculty of Science, Tohoku University, Aoba-ku, Sendai 980*

(Received March 25, 1992)

Optical conductivity ($\sigma$) and photoelectron spectrum of rare-earth hexaborides were measured at room temperature to investigate its electronic structure. The origin of the peak structure in the $\sigma$-spectrum due to the interband transition of trivalent rare-earth hexaborides and $SmB_6$ was analyzed with an aid of the photoelectron data. In the photoelectron spectrum of $YbB_6$, clear peak structure due to the trivalent $Yb^{3+}$ state ($4f^{13}$ configuration) was resolved in addition to the main peak due to the divalent $Yb^{2+}$ state ($4f^{14}$ configuration). The gap energy in the divalent state was estimated to be 0.5 eV from the sharp rise in the $\sigma$-spectrum of which magnitude is comparable with the gap energy determined from the photoelectron data.

**KEYWORDS:** rare-earth hexaborides, optical conductivity, photoelectron spectrum, interband transition

## §1. Introduction

Rare-earth hexaborides ($RB_6$) crystallize in the CsCl type in which the octahedron molecule of $B_6$ replaces Cl and rare-earth atom (R) occupies the Cs-site. According to the calculation of the molecular orbital structure of the $RB_6$,[1] the $2s$-$2p$ bonding and nonbonding states form the main part of the valence band, and the $2s$-$2p$ antibonding state forms the main part of its conduction band. In the trivalent $RB_6$, the $5d$ electron ($E_g$ state) supplied by the R ion comes across the Fermi energy ($E_F$) and becomes the conduction electron. The $4f$ state of the R ion modifies this main band scheme and the grade of the modification of the electronic band structure by the $4f$ state gives rise to an interesting physical properties such as a valence Fluctuation ($SmB_6$), a dense Kondo state ($CeB_6$) and so on. Recent theoretical work on the band calculation of $LaB_6$[2] confirmed this band picture.

Our interests on the peak structure in the $\sigma$-spectrum of $RB_6$ are in the following three points: (1) the structure in the far-infrared region due to a gap formation of $SmB_6$ at low temperature, (2) an anomalous infrared absorption which have been recently found to exist in common with all trivalent $RB_6$ compounds together with $SmB_6$ at the energy region of 0.5–0.7 eV, and (3) the interband transition in the vacuum ultraviolet region which gives us information on its overall electronic band structure.

The discussion on the first point (1) will be given in a separated paper. The discussion on the second point (2) has been already given in a separated paper.[3] In the present paper, we report our recent analysis of the experimental results on (3) obtained from the optical conductivity and the relevant photoelectron measurements.

## §2. Experimental

### *a. Sample*

Single phased crystals of rare-earth hexaboraides were grown by a floating zone method. The sample surface for the reflection measurement was mirror-polished with carborundum and alumina powder. The surface for the vacuum ultraviolet photoelectron (UPS) measurement was cleaned by filing work in an ultra high vacuum sample preparation chamber ($<1\times10^{-10}$ Torr) just before the measurement so that the oxygen O$2p$ signal at the binding energy of 6 eV disappeared.

### *b. σ- and UPS spectrum*

Reflectivity measurement was done in a wide energy range 3 meV–40 eV at 300 and 9 K. The observed reflectivity spectrum was extrapolated by each conventional function in the both energy sides: in the lower energy below 3 meV by a metallic reflectivity and in the higher energy region above 40 eV by a damping function proportional to $\omega^{-4}$ to obtain a $\sigma$-spectrum by a Kramers-Kronig (K-K) transformation.

Spectrum in the far-infrared region was measured at the synchrotron radiation (SR) facility, the UVSOR of the Institute for Molecular Science using a Martin-Puplett type Fourier spectrometer. The signal was detected by Ge or InSb bolometer. The reflectivity spectrum in the 4–40 eV region was measured at the beamline 1B and the UPS spectrum with the energy resolution of 0.3 eV was measured at the beamline 2B of the SR facility, the SOR in the Institute for Solid State Physics, the University of Tokyo. The SR light for the reflectivity measurement in the vacuum ultraviolet was monochromatized by a 1 m Seya-Namioka type monochromator and its intensity was detected by a photomultiplier. The reflectivity spectrum in the intermediate energy region between the far-infrared and the vacuum ultraviolet measured by an usual spectroscopic system in the laboratory using conventional light sources and detectors. The energy resolution ($dE/E$) was kept less than 5% in the whole energy region.

## §3. Results and Discussions

### *(i) Electronic structure of trivalent $RB_6$ and $SmB_6$*

Figure 1 shows the $\sigma$-spectrum of trivalent $RB_6$ and $SmB_6$ obtained by the K-K transformation of each reflec-

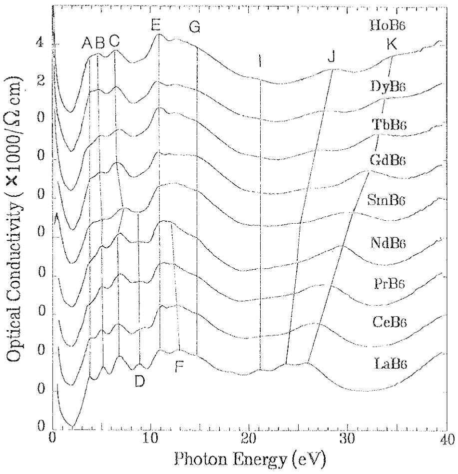

Fig. 1. Optical conductivity spectra of trivalent rare-earth hexaborides and $SmB_6$ at 300 K.

tivity spectrum. The sharp dip at 2 eV in the $\sigma$-spectrum is a so-called "plasma-window" which corresponds to an onset of an absorption due to a plasmon excitation in a metal. The lower energy part below the plasma-window corresponds to a metallic reflectivity, a so-called Drude reflection. The plasma-window for all trivalent $RB_6$ was found at the almost same energy. This means that the rare-earth $5d(E_g)$ state which forms the conduction band exists at the almost same energy position across the $E_F$ nearly independently of the R ion. The effective electron number contributing to the conductivity in $LaB_6$ was estimated to be almost one per unit cell[3] if we take the effective mass of $0.7\,m_0$ which is consistent with the band mass obtained by the dHvA measurement.[4]

In the $\sigma$-spectrum of $LaB_6$, eleven peaks were resolved. They are the A-peak (at 3.5 eV), B (5.3 eV), C (6.8 eV), D (9.0 eV), E (11.0 eV), F (12.5 eV), G (15.0 eV), H (18.0 eV), I (21.0 eV), J (23.5 eV) and K (25.5 eV). The origins of these peaks were assigned as Follows with the aid of the results of the band calculation,[2] its density-of-state (DOS) spectrum on $LaB_6$[5] and the relevant UPS measurement.

### *a. On the A, E, G and I peak*

As mentioned in §1, the overall electronic structure of the valence and the conduction band of $RB_6$ are determined by the boron network. Therefore, the peak of which energy position is almost insensitive to the sort of the R ion can be attributed to the intra-atomic transition of boron and to the rare-earth $5d(t_{2g})$ from the boron $2s$-$2p$ bonding state. According to the recent band calculation on $LaB_6$,[2,5] the peaks in the DOS spectrum of the boron $2s$-$2p$ bonding state distributes at 0–10 eV region and the $5d$ at 4–5 eV above the $E_F$. The all A, E, G and I peaks are attributed to the intra-atomic interband transition of the boron $2s$-$2p$ bonding state to the boron $2s$-$2p$ antibonding state.

### *b. On the B, C and D peak*

First, the B and C peaks were assigned to be due to the $2s$-$2p$(boron)-$5d$(rare-earth) interband transition because the two peaks showed a gradual red shift of 0.5 eV from La to Ho and a definite blue shift only in $SmB_6$. $SmB_6$ is a homogeneous valence fluctuating compound in which the ratio of $Sm^{2+}$ to $Sm^{3+}$ is about 4:6. In the divalent $Sm^{2+}$ state, $SmB_6$ is a semi-conductor and consequently the $5d$ state, which is crossing the $E_F$ in the trivalent $Sm^{3+}$ state, is pushed up apart from the $E_F$ level. This is the reason of the blue shift seen in $SmB_6$. Similar blue shift on the corresponding peaks was found also in $YbB_6$ which is fundamentally divalent. The D peak also was assigned to be due to the same interband transition with the B and C peak because the transition energy of 9 eV is consistent with the energy separation between the boron $2s$-$2p$ state at 5 eV below the $E_F$ and the rare-earth $5d$ $(t_{2g})$ state at 4 eV above the $E_F$ in the DOS spectrum of $LaB_6$.[5]

### *c. On the J and K peak*

As seen in the figure, the energy position of the J and K peak changes. The peak showed a large blue shift as the rare-earth ion becomes heavier from La to Ho. We measured the UPS spectrum of trivalent $RB_6$ to know the initial state of the interband transition corresponding to the J and K peak.

Figure 2 shows the energy distribution curves for $LaB_6$, $DyB_6$ and $HoB_6$ at the excitation energy of 100 eV. The data for $LaB_6$ agreed well with the data by Aono *et al.*[6] In $LaB_6$, the structure at the binding energy of 0–10 eV region below the $E_F$ are due to the structure in the DOS spectrum of the boron $2s$-$2p$ bonding and non-bonding states. In $LaB_6$, the peak at 17 eV corresponds to the $5p_{3/2}$ core hole state and the peak at 19.3 eV to the $5p_{1/2}$ (spin-orbit doublet). In the curve of $DyB_6$ and $HoB_6$, the two peak structure due to the spin-orbit splitting of the $4f$ core hole state with its multiplet in the valence band was resolved at 5.1 eV and 9.4 eV for $DyB_6$, and at 6.2 eV and 9.0 eV for $HoB_6$ of which peaks exist overlapping with the background spectrum composed of the boron $2s$-$2p$ bonding and non-bonding state barely seen in $LaB_6$. The peak at 23.1 eV for $DyB_6$ and at 24.1 eV for $HoB_6$ are the $5p_{3/2}$ state.

Figure 3 shows the plotting of the energy positions of

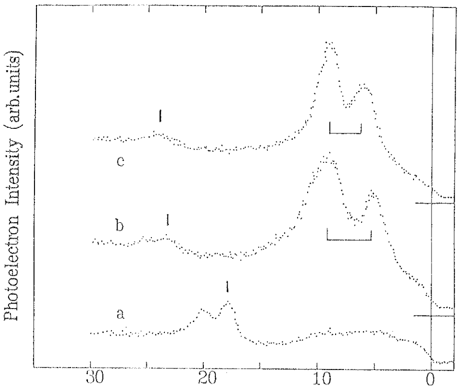

Fig. 2. Photoelectron spectra of $LaB_6$ (a), $DyB_6$ (b) and $HoB_6$ (c) at 300 K. Thick solid line in each curve shows the $5p_{3/2}$ core hole peak. Thin vertical line shows the $E_F$ position.

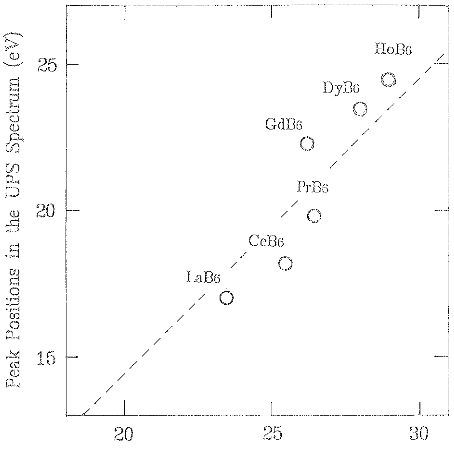

Fig. 3. The energy positions of the $5p_{3/2}$ peak in the UPS spectrum of some trivalent rare-earth hexaborides against the peak positions of the J peak in the $\sigma$-spectrum of the corresponding compound. Dashed line is drawn as a guide for the eyes.

the $5p_{3/2}$ peak in the UPS spectrum for each $RB_6$ against the energy positions of the J peak in the $\sigma$-spectrum of the corresponding $RB_6$. The peaks in both spectra showed an almost same amount of the energy shift (i.e. the slope of the curve is nearly one) and the energy difference between the peaks in both spectra is about 5 eV for each $RB_6$. This means that (1) the J peak is attributed to the interband transition from the rare-earth $5p_{3/2}$ state to the rare-earth $5d(t_{2g})$ state of which peak in the DOS-spectrum exists in common at about 4–5 eV above the $E_F$[5] and (2) consequently the $5d$ state which is the final state of the J and K peak exists at the same energy position in common with trivalent $RB_6$. This is consistent with the result of the $\sigma$-spectrum showing that the $5d$ position is almost same in all trivalent compounds. The energy separation between the $5p_{3/2}$ and the $5d$ states agrees with the J peak energy. The K peak is a spin-orbit pair of the $5p$ core state because the energy separation of the peaks J and K is nearly equal to the spin-orbit splitting energy of the rare-earth $5p$ state for each $RB_6$.

### *d. On the F peak*

In the $\sigma$-spectrum, the F peak showed a red-shift with decreasing its intensity and was immersed into the background intensity as the R ion becomes heavier from La to Nd. We assigned that the final state of the interband transition corresponding to the F peak is the unoccupied $4f$ state. It is known that the unoccupied $4f$ level approaches to the $E_F$ because of the incomplete Coulomb screening from the rare-earth atomic nucleus as the increase of the number of the occupied $4f$ electron. This is the reason for such red-shift of the F peak position. The number of the unoccupied $4f$ state decreases as the R ion becomes heavier. This is the reason for the decrease in intensity.

To know the energy position and its intensity of the unoccupied $4f$ state in the conduction band of $RB_6$ compound, the BIS (Bremstrahlen isochronic spectroscopy) spectrum, which is powerful tool to get directly the information on an unoccupied band, was measured for $LaB_6$, $TbB_6$, and $DyB_6$ by Suga *et al.*[7] For $LaB_6$ an intense and broad with the FWHM of 2.9 eV corresponding to the unoccupied $4f$ state was observed at 5.4 eV in addition to the broad peakless background spectrum which is composed of the rare-earth $5d$ and boron $2s$-$2p$ antibonding bands. The peak position shifted towards the $E_F$ with decreasing the intensity as the R ion becomes heavier from La to Dy. From these results, the final state of the interband transition corresponding to the F peak is considered to be the unoccupied $4f$ state. That is, the F-peak is the interband transition from the boron $2s$-$2p$ bonding state which exists at 6 eV below the $E_F$ in common with all $RB_6$ to the unoccupied $4f$ state.

### *(ii) Electronic structure of $YbB_6$ near the Fermi level*

$YbB_6$ is considered to be divalent compound which shows in principle a semiconductor-like property. The measured electric resistivity, however, is metallic although the magnitude is smaller by the magnitude of two order than trivalent $RB_6$,[8] and the metallic behavior has been considered to be due to the existence of the small amount of the impurity like as a lattice defect. The low energy part of the optical conductivity spectrum of $YbB_6$ at 300 K is shown in Fig. 4. The sharp peaks at 13.7 and 108.3 meV at 300 K are due to the phonon absorption.[9] The plasma-window at 0.5 eV in the reflection spectrum at 300 K did not change its position even as the temperature decreased to 9 K. The energy is smaller by the factor of 4 than that of trivalent $RB_6$. Therefore, the number of the electrons contributing to the conductivity is more few by more than one order than a typical trivalent $RB_6$ if we assume the same effective mass ($m^*$) for the conduction electron because the plasma-frequency ($\omega_p$), which gives a plasma-window, is given by $\omega_p^2 = 4\pi e^2 N/m^*$. Here, N is the number of the conducting electrons per unit volume. The fact that the $\omega_p$ is independent on the temperature means that the conduction electrons are not thermally excited one to the conduction band but the almost same amounts of conduction electrons with at 300 K exist even at the low temperature.

To know the electronic structure near the $E_F$ of $YbB_6$, the UPS spectrum was measured at 300 K. The UPS spec-

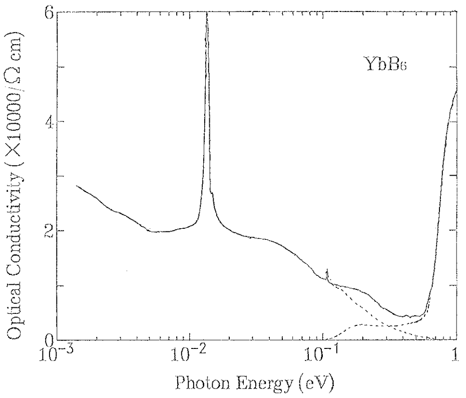

Fig. 4. The low energy part of the optical conductivity spectrum of $YbB_6$ at 300 K. The dashed curves show the decomposition of the spectrum into the Drude part and the interband transition part.

tra of $YbB_6$ at the excitation energy of 32 and 100 eV are shown by the curves (b) and (c), respectively, in Fig. 5. The spectrum of $LaB_6$ which is a good reference sample to know the $4f$ contribution to the spectrum is also shown in the curve (a). The $E_F$ position was calibrated by a usual way from the UPS spectrum of Au which was measured in the same apparatus.

The curve for $LaB_6$ shows the DOS spectrum of the boron $2s$-$2p$ bonding and antibonding state. The profile of the UPS spectrum (b) of $YbB_6$ at the excitation energy of 32 eV agrees well with that of $LaB_6$. The existence of the band gap for the $2s$-$2p$ state can be seen in the UPS spectrum of $LaB_6$ and the magnitude agrees with the result of the band calculation on $LaB_6$.[2,5] This means that the boron $2s$-$2p$ bonding state does not change with the sort of the rare-earth ion.

At the excitation energy of 100 eV which approaches to the threshold energy of the $4d$-$4f$ transition, however, the intense doublet structure appeared at the binding energy of 0–3 eV overlapping with the $2s$-$2p$ state seen in the curve (b). The intense doublet structure is due to the spin-orbit pair with the multiplet structure of the core hole state in the $4f^{14}$ configuration of the divalent $Yb^{2+}$. The important point is the existence of the intense structure at the binding energy of 6–12 eV. We assigned their peaks to be due to the trivalent $Yb^{3+}$ state. If so, the ratio of $Yb^{3+}$ to $Yb^{2+}$ is about 1:4 from the ratio of the crossectional areas of the two bands. This value is comparable with that obtained by the similar way from the XPS data given by Iga *et al.*[10] Iga *et al.* reported similar structure at the same energy region in the XPS spectrum of $YbB_6$ and concluded that the structure originates from the existence of the $Yb_2O_3$ compound which was trivially formed at the surface due to the sample oxidization. In our case, the sample was prepared in good conditions and we don't think that the peak structure at the 6–10 eV region is due to the oxidization. Recently, the same structure was reported by Kakizaki *et al.* in the UPS spectrum of $YbB_6$[11] and they referred to the possibility that such structure at the binding energy of 6–12 eV region might be due to the surface induced $Yb^{3+}(4f^{13})$ state with multiplet structure. Another type of experiment, for example, Mossbauer isomer shift measurement will be useful to determine if the trivalent $Yb^{3+}$ exist as an intrinsic property in $YbB_6$.

Anyway, at present, we consider that the $4f$ electron in the major divalent state ($4f^{14}$ configuration) and the $5d$ electron in the minor trivalent state crosses the $E_F$ level and contributes to the metallic electric resistivity as well as the Drude part of the $\sigma$-spectrum of $YbB_6$.

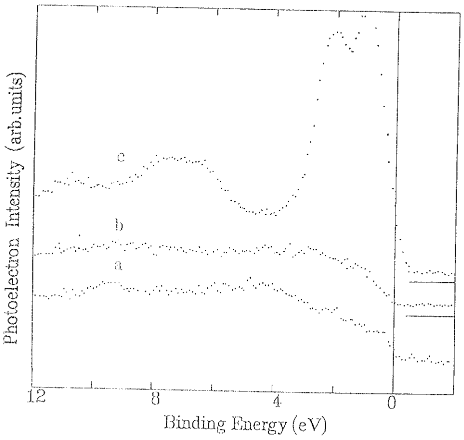

Fig. 5. The photoelectron spectra of $YbB_6$ at 300 K at the excitation energy of 32 eV (b) and 100 eV (c). For comparison, the spectrum of $LaB_6$ at 300 K at the excitation energy of 32 eV is shown also in the curve (a).

## Acknowledgements

The authors express their thanks to Dr. K. Soda of College of Engineering of University of Osaka Prefecture and Ms. T. Mori of the SOR-RING of Institute for Solid State Physics, the University of Tokyo for their supports to the UPS measurement at the BL2 at the SOR. They thank also Mr. M. Tomikawa of Kobe University for his help during the experiment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 02216101) by the Ministry of Education, Science and Culture.

## References

1) H. C. Longuet-Higgins and M. de V. Roberts: Proc. Roy. Soc. **224** (1954) 336.
2) H. Harima, O. Sakai, T. Kasuya and A. Yanase: Solid State Commun. **66** (1988) 603.
3) S. Kimura, T. Nanba, S. Kunii and T. Kasuya: Solid State Commun. **75** (1990) 717.
4) Y. Onuki, T. Komatsubara, P. H. Reinders and M. Springford: J. Phys. Soc. Jpn. **58** (1989) 3698.
5) S. Kimura, T. Nanba, S. Kunii and T. Kasuya: J. Phys. Soc. Jpn. **60** (1991) 745.
6) M. Aono, T.-C. Chiang, J. A. Knapp, T. Tanaka and D. E. Eastman: Phys. Rev. **B21** (1980) 2661.
7) S. Suga *et al.* (Osaka University): private communication.
8) J. M. Tarascon *et al.*: J. Appl. Phys. **51** (1980) 574.
9) S. Kimura, T. Nanba, S. Kunni and T. Kasuya: J. Phys. Soc. Jpn. **61** (1992) 371.
10) F. Iga *et al.*: Solid State Commun. **50** (1984) 903.
11) A. Kakizaki *et al.*: Tech. Report of ISSP (University of Tokyo) Ser. A No. 2428 (1991).