Optical spectroscopy study on the electronic structure of Eu$_{1-x}$Ca$_x$B$_6$

Jungho Kim and S.-J. Oh
School of Physics Center for Strongly Correlated Materials Research,
Seoul National University, Seoul 151-742, Republic of Korea

Youngwoo Lee and E. J. Choi*
Department of Physics, University of Seoul, Seoul 130-743, Republic of Korea

C. C. Homes
Department of Physics, Brookhaven National Laboratory, Upton, NY 11973-5000

Jong-Soo Rhyee and B. K. Cho
Center for Frontier Materials and Department of Materials Science and Engineering,
K-JIST, Gwangju 500-712, Korea

The optical conductivity $\sigma_1(\omega)$ of Eu$_{1-x}$Ca$_x$B$_6$ has been obtained from reflectivity and ellipsometry measurements for series of compositions, $0 \leq x \leq 1$. The interband part of $\sigma_1(\omega)$ shifts continuously to higher frequency as Ca-content $x$ increases. Also the intraband spectral weight of $\sigma_1(\omega)$ decreases rapidly and essentially vanishes for $x \geq x_c = 0.35$. These results show that the valence band and the conduction band of Eu$_{1-x}$Ca$_x$B$_6$ move away from each other such that their band overlap decreases with increasing Ca-substitution. As a result, the electronic state evolves from the semimetallic structure of EuB$_6$ to the insulating CaB$_6$ where the two bands are separated to open a finite gap ($\approx 0.25$ eV) at the X-point of the Brillouin zone.

PACS numbers: 71.20.-b, 71.30.+h, 78.20.-e

The divalent hexaboride compounds RB$_6$ ($R=$ Eu, Ca, Sr, etc) have drawn much attention for the last decade due to their interesting electrical and magnetic properties. These materials crystalize in a cubic structure with boron octahedra in the center of the unit cell and the cations sitting on the corners of the cube. In EuB$_6$, the Eu ions ($S = 7/2$) exhibit a ferromagnetic alignment at $T_C = 15$ K. This transition accompanies a large drop of dc-resistivity. In addition, the infrared reflectivity measurement showed an unusual shift of the plasma frequency across the transition. The resistivity and the plasma frequency changes are also induced by external magnetic field.

The hexaboride CaB$_6$ is isovalent with EuB$_6$. However, the low-temperature dc-resistivity exhibits a semiconducting temperature dependence, in contrast with the metallic behavior of EuB$_6$. While the Ca ion bears no magnetic moment, weak ferromagnetism was observed at high temperature ($T_C \sim 600$ K) in the lightly La-doped Ca$_{1-x}$La$_x$B$_6$ as well as in the nominally stoichiometric CaB$_6$ compound. Various explanations of this effect such as the excitonic state model and the dilute electron gas model have been proposed. The effect is also attributed to extrinsic origin such as structural defect or impurities.

As a prerequisite to the understanding of these unconventional phenomena, the band structure of EuB$_6$ and CaB$_6$ were extensively studied both theoretically and experimentally. de Haas-van Alphen (dHvA) and Shubnikov de Hass (SdH) experiments show a semimetallic band structure in both materials, i.e., both electron pocket and hole pocket exist on the Fermi surface. On the other hand, angle resolved photoemission spectroscopy (ARPES) and soft x-ray emission measurements showed that in both compounds the bands are separated with a sizable gap of $\sim 1$ eV. Theoretically, the early local-density approximation (LDA) band calculation predicted that, in EuB$_6$ and CaB$_6$, conduction band (CB) overlaps with valence band (VB) at X point of the Brillouin zone. LDA+U calculation result for EuB$_6$ agrees with this semimetallic band structure. However, for CaB$_6$, pseudo-potential GW and also WDA calculation claim an insulating state with a sizable band gap of 0.8 eV. On the contrary, all electron GW calculation by Kino et al. shows that CaB$_6$ does not have such a large gap. A full-potential LMTO calculation yields a moderate gap of 0.3 eV. This lack of consistency among different results suggests that the band structure depends much on the details of the employed calculation methods.

Recently, Rhyee et al. have prepared a series of Eu$_{1-x}$Ca$_x$B$_6$ where Eu is gradually replaced by the isovalent Ca. As the Ca-content $x$ increases, the metallic dc-resistivity $\rho(T)$ was found to increase and then crosses over to an insulating behavior. Noting that no carrier doping is expected in this series of isovalent samples, the evident changes of the electrical properties imply a non-trivial effect of the Ca-substitution. Also, this system provides an opportunity to understand, when com-
FIG. 1: Reflectivity spectra of Eu$_{1-x}$Ca$_x$B$_6$ for various values of $x$ from $x = 0$ (EuB$_6$) and $x = 1$ (CaB$_6$) taken at room temperature.

FIG. 2: Optical conductivity $\sigma_1(\omega)$ of Eu$_{1-x}$Ca$_x$B$_6$ for: (a) wide-range of frequency up to 5 eV; (b) low-frequency infrared region. In (a), the curves are uniformly displaced along the vertical axis to avoid heavy overlap among them. Inset shows $\sigma_1(\omega)$ of EuB$_6$ and CaB$_6$ without the vertical shift.

In this study, we have performed a wide range ($20 - 50000$ cm$^{-1}$) optical spectroscopic measurement of Eu$_{1-x}$Ca$_x$B$_6$ for a series of compositions $x$ which ranges from 0 to 1. The single-crystal samples were synthesized by a boro-thermal method as described in detail elsewhere. Boron powder of 99.9% purity was used. To determine the Eu content $x$, we measured the dc-magnetization $M(H)$ of each sample until it saturates at high magnetic field $H$. The saturation value is proportional to $x$, from which we find $x = 0, 0.13, 0.25, 0.35, 0.54$ and 1. Dc-resistivity and Hall coefficient of these samples were reported in the earlier publication. For present optical study, crystals from the same sample batches were used. The reflectance $R(\omega)$ at a near-normal angle of incidence was measured at 300 K in the $20 - 5000$ cm$^{-1}$ and $5000 - 50000$ cm$^{-1}$ ranges using a Fourier transform spectrometer with an in situ overcoating technique and a grating spectrometer with a V-W method, respectively. The crystals were wedged by 2° to avoid internal interference effect.

Figure 1 shows the reflectivity of Eu$_{1-x}$Ca$_x$B$_6$ over the wide range of frequency. In the low energy infrared region, the spectra exhibit a large change with $x$. For $x = 0$ (EuB$_6$), $R(\omega)$ is high and shows a plasma edge at $\omega \sim 1200$ cm$^{-1}$, which is similar to the earlier observation by Degiorgi et al. As $x$ increases, the reflectivity level decreases and the plasma edge shifts continuously toward lower frequency. For $x \geq 0.35$, this metallic feature of $R(\omega)$ is significantly suppressed and the phonon peak at 150 cm$^{-1}$ becomes prominent. The absorption peaks at high energy ($\omega > 10^4$ cm$^{-1}$) correspond to interband excitations.

The real part of the optical conductivity $\sigma_1(\omega)$ has been determined from a Kramers-Kronig analysis of the measured reflectance, for which extrapolations for $\omega \rightarrow 0$ and $\infty$ must be supplied. For $\omega \rightarrow 0$, the Hagen-Rubens (HR) extrapolation was employed. Above the highest measured frequency, a free-electron approximation $R(\omega) \propto \omega^{-4}$ was assumed. For $1.5 \leq \omega \leq 5.5$ eV, an ellipsometer (Sopra GES5) was used to directly determine $\sigma_1(\omega)$. The result showed a good agreement with the reflectance measured in the same region.

Figure 2(a) displays the overall structure of $\sigma_1(\omega)$ on a linear scale. To allow for a clearer presentation, the curves are displaced uniformly along the vertical axis. The conductivity $\sigma_1(\omega)$ consists of a gradual rise up to $\simeq 2.5$ eV and two prominent peaks at 2.7 and 3.7 eV, respectively. Also a weak absorption appears at about 1.5 eV. Note that the 2.7 eV peak shifts to higher energy as $x$ increases, as indicated by the arrows. A similar shift occurs with the 3.7 eV peak as well. The inset displays $\sigma_1(\omega)$ of $x = 0$ and 1 without the vertical displacement. Note that the shift occurs over the wide energy range, including the region of the gradual rise.

We assign the observed $\sigma_1(\omega)$, the rise and the peaks, to interband transitions of Eu$_{1-x}$Ca$_x$B$_6$. Band structure calculations show that in EuB$_6$, the CB width is about 3 $\sim$ 4 eV and the band bottom is formed at the X point of the Brillouin zone (BZ). The VB top is located at the same point. Most of the calculations show that, in EuB$_6$, the two bands overlap by small amount to form
a semimetallic state. An optical excitation from the VB to the CB will then occur over a broad frequency from \( \omega = 0 \) to the maximal interband energy. For instance, according to Massidda et al., the 2.75 eV peak corresponds to the VB-CB excitation at the \( \Gamma \) point. The blue shift of \( \sigma_1(\omega) \) which occurs nearly uniformly over the wide frequency range implies that with Ca-doping, the VB-CB distance increases throughout the BZ.

In EuB\(_6\), the VB is formed by the B 2p level, while the CB is derived from the hybridization of the cation d (Eu 4d) and B 2p levels. As Ca is introduced, the lattice constant of Eu\(_{1-x}\)Ca\(_x\)B\(_6\) monotonically decreases. Also, within the unit cell, the cation-boron distance decreases and as a result, the hybridization will change. In addition, Eu\(^{++}\) has a larger ionic radius than Ca\(^{++}\) (1.12 Å vs 1.0 Å). These structural and chemical changes seem to contribute to the observed band shift. Further, Kuneš et al. showed that in EuB\(_6\), the Eu 4f state, through hybridization with B 2p state, has significant consequences in the band structure, particularly at X point of BZ. It will be interesting to perform a complete band structure calculation of Eu\(_{1-x}\)Ca\(_x\)B\(_6\) to see whether the observed band shift is reproduced, and also to find which effect plays the major role of it. As for the 1.5 eV peak, Caimi et al. assigned it to the intra-atomic Eu 4f \( \rightarrow \) 5d transitions. This is consistent with the absence of the peak in CaB\(_6\).

In Fig. 2(b), we show the low-frequency part of the spectrum. The sharp peaks at \( \omega \approx 146 \) and 858 cm\(^{-1}\) represent infrared-active phonons. The rapid increase of \( \sigma_1(\omega) \) at low-frequency with decreasing \( \omega \) represents the metallic response of free carriers. This intraband conductivity decreases with \( x \) and is suppressed to a negligible amount for \( x \geq 0.35 \), indicating that the metallic carriers disappear. We estimate the spectral weight of \( \sigma_1(\omega) \) in terms of the plasma frequency \( \omega_p \) using the relation \( \omega_p^2 = \frac{4\pi e^2}{m^*} \int_{0}^{\infty} \sigma_1(\omega) d\omega \). Here the cut-off frequency \( \omega_c \) for the integration was taken as 2000 cm\(^{-1}\). The phonon contribution was subtracted from the sum. The result is shown in Fig. 3 which will be discussed later. Additionally, we note that the intraband \( \sigma_1(\omega) \) does not follow the conventional Drude form. Perucchi et al. analyzed it as a sum of several Drude components.

In EuB\(_6\), the metallic carrier creation is attributed to an extrinsic origin such as a boron vacancy or to the intrinsic semimetallic CB-VB overlap. Degiorgi et al. measured reflectivity of an independent EuB\(_6\) sample. The plasma edge in that work coincides with ours, suggesting that the carrier density is same. In the present work, the plasma frequency changes systematically in Ca-doped samples. It is less likely that these results come from uncontrolled random vacancies. As for the latter scenario, which seems more plausible at this point, the carrier density depends on the amount of the band overlap at X-point. The \( x \)-dependence of \( \omega_p \) shows that the overlap decreases with Ca-doping. For \( x \geq 0.35 \), it is inferred that CB and VB are separated.

To test this picture more directly, let us give a closer look at the onset of the interband conductivity which corresponds to the VB-CB excitation at X point. In Fig. 3 we show \( \sigma_1(\omega) \) in the mid-infrared region for four samples, one below \( x_c \) (\( x = 0.25 \)) and the rest at \( x \geq x_c \). For a clearer presentation, the curves have been displaced vertically. The interband \( \sigma_1(\omega) \) appears as a linear rise with increasing \( \omega \) on the high energy side of the spectra. For the samples with \( x \geq 0.35 \), we extrapolate along the linear region to find the onset energy \( \Delta \), as shown by the dashed lines. At \( x = 1 \) (CaB\(_6\)), \( \Delta \) is about 0.25 eV. The Drude feature in the far-infrared region represents perhaps residual impurity-induced carriers. At \( x = 0.54 \) and 0.35, \( \Delta \) is smaller. For these two samples, \( \Delta \) determination is somewhat uncertain due to the remnant \( \sigma_1(\omega) \) at \( \omega < \Delta \). At \( x = 0.25 \), the interband \( \sigma_1(\omega) \) is strong. Various model functions fit to the intraband \( \sigma_1(\omega) \) were evaluated, but depending on the fitting details, \( \Delta \) varied from 0 to as large as 0.2 eV. The inset illustrates a fit with \( \Delta = 0 \) which corresponds to the case where the bands overlap. The large uncertainty of \( \Delta \) makes it difficult to determine the X-point band state for \( x < 0.35 \).

In Fig. 3 we summarize the observed optical changes of the 2.7 eV peak position \( \Omega \), the squared plasma frequency \( \omega_p^2 \) and the interband onset frequency \( \Delta \). The \( \Omega \) in CaB\(_6\) (=3.35 eV) is about 0.6 eV higher than in EuB\(_6\). Mean-while, the band overlap in EuB\(_6\) estimated from the band calculation is about 0.3 eV. If the bands move rigidly throughout the BZ, the X-point separation at \( x = 1 \) will be 0.3 eV. This is close to the observed \( \Delta = 0.25 \) eV of CaB\(_6\). Also the bands will fall apart (\( \Delta = 0 \)) when the shift is 0.3 eV. This occurs, from Fig.4(a), at \( x = 0.35 \), which agrees with the suppression of \( \omega_p^2 \). However, \( \Delta \) at this composition (= 0.15 eV) is rather significant. It
In (b), \( \omega \) frequency with \( x \) faster than the other part of may indicate that the gap opens quickly, i.e, between the values are indicated together. The observations (a) Position of the 2.7 eV peak. (b) Squared plasma \omega^2 \) is converted into carrier density \( n \) (right axis) from \( \omega^2 = 4\pi ne^2/m^* \) using \( m^* = 0.25 \) [ref.18 and 19]. Error bars of the values are indicated together.

may indicate that the gap opens quickly, i.e, between \( x = 0.25 \) and 0.35, the band shift at the X-point occurs faster than the other part of \( x \). Interestingly, the change of \( \Omega \) shows a rapid shift for this \( x \) range. However, due to the uncertainty of \( \Delta \) at \( x = 0.35 \), it is difficult to draw the exact \( x \)-dependence of the gap opening. Nevertheless, the overall behaviors of the three optical conductivity features show consistently that the electronic structure transition occurs from the semimetallic EuB\(_6\) to the insulating CaB\(_6\) through the band shift. EuB\(_6\) exhibits a ferromagnetic transition at \( T_c = 15 \) K. It was found that \( T_c \) decreases with Ca-substitution and then, interestingly, disappears at \( x_c \). This correlation suggests that the ferromagnetism is coupled with the charge carrier. A quantitative analysis of this relationship will be discussed in an independent paper.

In summary, we have performed reflectivity and ellipsometry measurements on the isovalent hexaboride series compounds Eu\(_{1-x}\)Ca\(_x\)B\(_6\) (0 \( \leq \) \( x \) \( \leq \) 1) over wide energy range of 2.5 meV - 6 eV and found that the optical conductivity exhibits systematic evolutions from EuB\(_6\) to CaB\(_6\). The interband \( \sigma_1(\omega) \) including the two peaks at 2.7 eV and 3.7 eV shifts continuously to higher energy as \( x \) increases. This shows that, along with the cation substitution, the valence band and the conduction band move away from each other throughout the Brillouin zone and the VB to CB energy distance increases with the Ca-content. As for the the low-frequency intraband \( \sigma_1(\omega) \), the Drude spectral weight decreases continuously with \( x \) and suppressed for \( x > 0.35 \). In EuB\(_6\), we adopted the semimetallic band structure calculation results and showed that the observed behaviors of the low frequency \( \sigma_1(\omega) \) are most readily explained in terms of the band shift at the X point of BZ. The carrier density decreases due to the decrease of the CB-VB overlap. At higher \( x \), the two bands are separated to open a band gap, which is consistent with the optical absorption onset at finite frequency, 0.25 eV in CaB\(_6\). As we mentioned in the introduction, extensive efforts have been made to calculate the band structure of EuB\(_6\) and CaB\(_6\). The observations of the present work, i.e, the systematic evolution of the electronic structure along with the cation substitution in Eu\(_{1-x}\)Ca\(_x\)B\(_6\) provide a strong constraint on the band structure calculations and should guide future works toward the complete understanding of the hexaboride compounds.

This work was supported by the KRF Grant No. 2002-070-C00032 and the KOSEF through CSCMR. Work at Brookhaven National Laboratory was supported by the DOE under Contract No. DE-AC02-98CH10886.

FIG. 4: The changes of the optical features of Eu\(_{1-x}\)Ca\(_x\)B\(_6\) with \( x \). (a) Position of the 2.7 eV peak. (b) Squared plasma frequency \( \omega^2 \). (c) Absorption onset of the interband transition.

1 B. T. Matthias, T. H. Geballe, K. A. adn E. Corenzwit, G. W. Hull, and J. P. Maita, Science 159, 530 (1968).
2 M. Kasaya, J. M. Tarascon, J. Etourneau, and P. Hagenmuller, Mater. Res. Bull. 13, 1055 (1978).
3 Z. Fisk, D. C. Johnston, B. Cornut, S. von Molnar, S. Osacroff, and R. Calvo, J. Appl. Phys. 50, 1911 (1979).
4 L. Degiorgi, E. Felder, H. R. Ott, J. L. Sarrao, and Z. Fisk, Phys. Rev. Lett. 79, 5134 (1997).
5 S. Broderick, B. Ruzicka, L. Degiorgi, H. R. Ott, J. L. Sarrao, and Z. Fisk, Phys. Rev. B 65, 121102 (2002).
6 D. P. Young, D. Hall, M. E. Torelli, Z. Fisk, J. L. Sarrao, J. D. Thompson, H. R. Ott, S. B. Osacroff, R. G. Goodrich, and R. Zysler, Nature (London) 397, 412 (1999).
7 M. E. Zhitomirsky, T. M. Rice, and V. I. Anisimov, Nature (London) 402, 251 (1999).
8 L. Balents and C. M. Varma, Phys. Rev. Lett. 84, 1264 (2000).
9 V. Barzykin and L. P. Gorkov, Phys. Rev. Lett. 84, 2207 (2000).
10 S. Murakami, R. Shindou, N. Nagaosa, and A. S. Mishchenko, Phys. Rev. Lett. 88, 126404 (2002).
11 S. Murakami, R. Shindou, N. Nagaosa, and A. S. Mishchenko, Phys. Rev. B 66, 184405 (2002).
12 D. Ceperley, Nature (London) 397, 386 (1999).
13 G. Ortiz, M. Harris, and P. Ballone, Phys. Rev. Lett. 82, 5317 (1999).
14 J. L. Gavilano, S. Mushkolaj, D. Rau, H. R. Ott, A. Bianchi, D. P. Young, and Z. Fisk, Phys. Rev. B 63,
In fact, in Ref. 23, the authors calculated the band structure of EuB$_6$ and CaB$_6$ using the LDA method. The result shows that the VB-CB distance at Γ point is smaller in CaB$_6$ by about 0.5 eV, contrary to the observation.

35 G. Caimi, S. Broderick, H. R. Ott, L. Degiorgi, A. D. Bianchi, and Z. Fisk, Phys. Rev. B 69, 012406 (2004).

36 P. Vonlanthen, E. Felder, L. Degiorgi, H. R. Ott, D. P. Young, A. D. Bianchi, and Z. Fisk, Phys. Rev. B 62, 10076 (2000).

37 A. Perucchi, G. Caimi, H. R. Ott, L. Degiorgi, A. D. Bianchi, and Z. Fisk, Phys. Rev. Lett. 92, 067401 (2004).

38 We have confirmed that $\sigma_1(\omega)$ in this energy range is insensitive to the low frequency extrapolation of the Kramers-Kronig transformation.

39 J.-S. Rhyee, B. H. Oh, B. K. Cho, M. H. Jung, H. C. Kim, K. Yoon, J. H. Kim, and T. Ekino, cond-mat/0310068.

40 Jungho Kim and Eunjip Choi (unpublished).