Infrared studies of $f$ electron systems under high pressure using synchrotron radiation

H. Okamura$^1$, M. Matsunami$^2$, R. Kitamura$^1$, S. Ishida$^1$, A. Ochiai$^3$, and T. Nanba$^1$

1 Graduate School of Science, Kobe University, Kobe 657-8501, Japan
2 Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan
3 Center for Low Temperature Science, Tohoku University, Sendai 980-8578, Japan
E-mail: okamura@kobe-u.ac.jp

Abstract. Infrared spectroscopic studies of various rare-earth compounds ($f$ electron systems) have been made under high pressure, in order to probe their interesting electronic structures induced by pressure. High pressures have been generated with the use of diamond anvil cells (DAC’s). To precisely perform IR reflectivity measurements of single crystal samples mounted in a DAC, the synchrotron radiation at SPring-8 has been used as a highly bright IR source. In this manuscript, the basic concept of the high pressure IR experiment using synchrotron radiation is introduced, and an example of obtained data for YbS and their physical interpretation are briefly discussed.

1. Introduction

Infrared (IR) spectroscopy has been a powerful tool to study the microscopic carrier dynamics and electronic structures in strongly correlated electron systems (SCES’s), such as rare earth ($f$ electron) compounds [1, 2, 3, 4, 5, 6, 7, 8] and transition metal ($d$ electron) compounds [9, 10, 11]. This is because various low-energy excitations and energy gaps, which play important roles in their unique physical properties, have energy scales in the range of IR photons (0.01-0.5 eV). In addition, the IR technique can be applied to a sample under high pressure using a diamond anvil cell (DAC), owing to the transparency of diamond over most of the IR region. This is also a great advantage of IR technique in comparison with other common spectroscopic techniques such as the photoemission and tunneling spectroscopies, since these latter techniques cannot be performed on a sample sealed in a pressure cell such as DAC.

IR spectroscopy of SCES’s under pressure is, however, technically challenging since the limited sample space available in a DAC allows only small sample sizes (50-200 μm). In addition, a high quality sample of SCES is generally a single crystal with metallic characteristics, so that an IR study cannot be done under a transmission configuration or with powder samples. Instead, a reflection configuration must be used with a small single crystal, and the reflectivity of the sample must be determined relative to a reference material whose reflectivity spectrum is already known. Given the restricted sample space and optical path in a DAC, such a reflectivity study with a single crystal sample is much more difficult than a transmission (absorption) study with powder samples. This is particularly the case with a conventional (thermal) IR source due to its low brightness. In the far-IR region (10 meV-0.1 eV), which is quite important in identifying...
the low-energy electronic structures in SCES’s, the above difficulty with thermal source becomes very significant due to the strong diffraction associated with the long wavelength.

To overcome the above difficulty, an apparatus for high pressure IR studies, which uses synchrotron radiation (SR) as a highly bright IR source, has been developed at SPring-8. This apparatus has made it possible to accurately perform IR reflectivity studies of single crystal samples in both far-IR (FIR) and mid-IR (MIR) regions under high pressure and at low temperature. Using this apparatus, we have performed IR reflectivity studies of several Ce and Yb compounds under pressure up to 40 GPa, at temperatures down to 5 K, in the photon energy range 15 meV -1.2 eV (120 - 10000 cm\(^{-1}\)). Below we will first describe the high-pressure IR apparatus at BL43IR, then will present an example of obtained results for YbS.

2. Experimental techniques

2.1. IR synchrotron radiation at SPring-8

The high pressure IR apparatus used in this work has been developed at the infrared beam line BL43IR of SPring-8.[12, 13] It consists of a custom-made IR microscope, a Bruker 120HR Fourier transform IR interferometer (FT-IR), and a DAC system. The microscope has a pair of reflective objectives (Schwarzschild mirrors) with a large working distance (WD) of 100 mm between them. This large WD has been intended to secure enough space for low-temperature DAC uses with a cryostat, as well as high-temperature DAC uses with a heating system for the earth science. Due to the large WD, the magnification of the microscope is \(8 \times\), which is low compared with those used in commercially available IR microscopes (generally 15-36\( \times\)). Despite this low magnification, the high brightness of the IR-SR has resulted in a nearly diffraction-limited beam size: without placing an aperture in the optical path, beam diameters of \(\sim 15 \mu m\) and \(\sim 30 \mu m\) were obtained in the mid- and far IR, respectively, at the sample position. In addition to the small beam size, the flux density (light intensity per unit area) in the mid-IR was two orders of magnitude greater than that from a thermal source (globar) contained in the FT-IR [12, 13]. Furthermore, this microscope covers the entire IR region (from FIR to visible) without changing any optical component, for both reflection and transmission configurations.

2.2. IR experiments with DAC

The diamond anvils used in this work were of type IIa with culet diameters of 400 \(\mu m\) (for pressures up to 40 GPa), 600 \(\mu m\) (up to 20 GPa) and 800 \(\mu m\) (up to 10 GPa). Commercially available diamond anvils are classified into several types, including types Ia, IIa, etc, based on the density of N (nitrogen) impurities contained. For IR studies, it is crucial to use a type IIa diamond anvil with a low density of N impurities, since a type Ia anvil with a higher density of N impurities generally have a strong absorption at 1100-1400 cm\(^{-1}\) range and below, as shown in Fig. 1. The spectral range of N absorption seen for type Ia diamond, which corresponds to a photon energy of \(\sim 0.15\) eV, is quite important for the study of strongly correlated electron systems, since key spectral features due to energy gaps and carrier dynamics often appear in this spectral range. In addition, a broad absorption is present at 1600-4000 cm\(^{-1}\) for both types of diamond, which is due to two-phonon absorption. A measurement is difficult in the region 1900-2250 cm\(^{-1}\) where this absorption is particularly strong. (Note that the IR light has to transmit the diamond anvil twice in the actual experiment.) Otherwise, the transmittance is high enough for IR spectroscopic studies, including the FIR region not shown in Fig. 1. (For reflection experiments, one of the anvils that does not transmit the infrared light can be a type Ia anvil, which is mechanically as strong as a type IIa.)

The DAC used in this work was of gas-driven type, with an accepting angle of 60 degrees for the incident (and reflected) IR beam. Figure 2 schematically shows the configuration for the reflectivity measurement with a DAC, and the mounting of the sample. A small single crystal sample (either polished or cleaved) was mounted directly on the culet face of one of
Figure 1. Mid-infrared transmittance spectra of type IIa and type Ia diamond anvils used in our laboratory, measured at room temperature. The height of the anvil was 1.7 mm, the culet diameter 0.6 mm, and the base diameter 3.1 mm. The absorption in the 1600-4000 cm\(^{-1}\) range seen for both types are due to two-phonon absorption, and that seen below 1400 cm\(^{-1}\) for the type Ia anvil is due to N (nitrogen) impurities. These spectra were measured at the sample position of a FT-IR, without using a microscope. The IR beam was incident on the base face of the anvil through an aperture of 2 mm diameter. The spectrum thus measured was normalized by that measured without the anvil, resulting in the transmittance spectra shown above.

Figure 2. Schematic diagram for the experimental configuration of IR reflectivity measurement in a DAC. A sample is placed directly on the culet face of a diamond anvil, and a gold film is also mounted as a reference mirror of the reflectivity. A few small ruby pieces are also mounted for monitoring the pressure through its fluorescence. In addition, a gold film was placed between the gasket and the culet face of the diamond anvil as a reference of the reflectivity. Small ruby pieces were also mounted for monitoring the pressure through the fluorescence method. They were sealed with a gasket (tension-annealed plate of stainless steel 301) and a pressure transmitting medium (fluorinert or glycerin). (Note that glycerin has recently been shown to have a fairly good hydrostaticity...
as a pressure medium [14, 15].) For low temperature measurements, the DAC was mounted in an optical cryostat (liquid He continuous flow type), with BaF$_2$ and polyethylene windows for MIR and FIR regions, respectively.

Since the reflectivity under high pressure was measured only below 1.2 eV, and since it was measured relative to diamond having a refractive index of $n=2.4$ (rather than the usual case of vacuum with $n=1$), the Kramers-Kronig analysis could not be used to derive the optical conductivity. We therefore used a Drude-Lorentz spectral fitting of the reflectivity spectra, taking into account the diamond refractive index, to derive the optical conductivity. This will be discussed again later.

3. Pressure-induced semiconductor-to-metal transition in YbS [18]

YbS at ambient pressure is an ionic insulator (Yb$^{2+}$S$^{2-}$) with the NaCl crystal structure, and has a band gap of about 1.4 eV [19, 20]. A previous optical study [19] showed that the band gap of YbS decreased under increasing external pressure. The extrapolation of the shifts of the fundamental absorption edge with pressure suggested a gap closing at $\sim 10$ GPa. In addition, volume compression data [19] and X-ray absorption data [20] suggested that the Yb mean valence in YbS increased from 2 above 10 GPa, and reached $\sim 2.4$ at 20 GPa. Namely, YbS above 10 GPa was in an intermediate-valence (IV) state, where the valence of each Yb ion is fluctuating between 2 and 3. However, since the previous optical study was performed at photon energies above 0.5 eV only, it was unclear whether or not the gap actually closed at $\sim 10$ GPa, and whether or not the IV state above 10 GPa was metallic. To answer these questions and to clarify the low-energy electronic structures of YbS under high pressure, we have carried out IR reflectivity studies of YbS over a photon energy range of 0.015-1.1 eV and a pressure range up to 20 GPa.

The samples used were single crystals grown with Bridgman method. A freshly cleaved surface of a small crystal was chosen, and it was mounted in the DAC as described above. The measurements were done at room temperature only.

Figure 3 shows $R(\omega)$ of YbS measured in a DAC under pressure, in both FIR and MIR regions. At low pressures below 8 GPa, the reflectivity is low, except for a single phonon peak near 30 meV. Such a spectrum is typical of an ionic insulator with the NaCl structure. Above 8 GPa, however, $R(\omega)$ increases rapidly with pressure, exhibiting a high reflection band below 0.3 eV. This is clearly due to plasma reflection, which shows that YbS above 8 GPa is metallic. With further increasing pressure above 10 GPa, $R(\omega)$ above 0.3 eV also increases significantly.

Figure 3. Reflectivity spectra of YbS measured in a DAC.[18] In these spectra, to clearly show the pressure-induced spectral changes, a weak spectral background due to multiple reflections from the sample and diamond surfaces has been subtracted. The spectra in a spectral region around 0.25 eV are not shown due to strong two-phonon absorption of the diamond as discussed in the text.
At 13 GPa and above, two marked dips are present in the spectrum. From these $R(\omega)$ spectra, we have derived the optical conductivity spectra $\sigma(\omega)$ using the Drude-Lorentz fitting [17], taking into account effects caused by the refractive index of the diamond (2.4), and a spectral background due to multiple reflections between the sample and diamond surfaces. (As already mentioned above, Kramers-Kronig analysis was not used here. The fitting procedure used is described in detail elsewhere [18].)

Figure 4 shows the obtained $\sigma(\omega)$ under pressure, together with that measured in the vacuum. The narrow peak below 0.1 eV, which are seen above 8 GPa, is a Drude peak due to free carriers. In addition, two pronounced absorption peaks are seen to grow with pressure above 10 GPa. Namely, the high pressure phase above 10 GPa is not a simple metal, but it has some peculiar features in the electronic structures near the Fermi edge. The detailed analyses of the data show that the carriers giving rise to the Drude peak has a large effective mass of the order of $10m_0$, where $m_0$ is the rest electron mass. It can be shown that the observation of the Drude peak due to such heavy electrons, and that of the pronounced absorption peaks, can be understood together using a model based on the hybridization of the $f$ state with a conduction band, which is also consistent with the IV previously observed above 10 GPa. A fuller account of the data analyses and discussions on the electronic structures of YbS are reported elsewhere [18].

Acknowledgments
We would like to thank Drs. T. Moriwaki and Y. Ikemoto for their assistance with experiments at SPring-8, and Dr. H. Yamawaki for providing the gasket materials used in this work. Experiments at SPring-8 have been performed under approval by JASRI (2005A0560-NSa-np, 2005B0621-NSa-np, 2006A1186-NSa-np, 2007B1314), and that at UVSOR by the Joint Studies...
Program of IMS.

References
[1] Degiorgi L 1999 Rev. Mod. Phys. 71 687
[2] Okamura H, Michizawa T, Nanba T and Ebihara T 2004 J. Phys. Soc. Japan 73 2045
[3] Matsunami M, Chen L, Takimoto M, Okamura H, Nanba T, Sekine C and Shirotani I 2005 Phys. Rev. B 72 073105
[4] Okamura H, Michizawa T, Nanba T, Kimura S, Iga F, Takabatake T 2005 J. Phys. Soc. Japan 74 1954
[5] Dordevic SV, Basov DN, Dilley NR, Bauer ED and Maple MB 2001 Phys. Rev. Lett. 86 684
[6] Hancock JN, McKnew T, Schlesinger Z, Sarrao JL and Fisk Z 2004 Phys. Rev. Lett. 92 186405
[7] Okamura H, Michizawa T, Nanba T, Ebihara T 2007 Phys. Rev. B 75 041101(R)
[8] Okamura H, Watanabe T, Matsunami M, Tsujii N, Ebihara T, Sugawara H, Sato H, Omuki Y, Isikakwa Y, Takabatake T and Nanba T 2007 J. Phys. Soc. Japan 76 023703, and references cited therein
[9] Okamura H, Matsunami M, Kimura S, Nanba T, Imai H, Shimakawa Y and Kubo Y 2001 Phys. Rev. B 64 180409(R)
[10] Okamura H, Koretsune T, Nanba T, Kimura S, Imai H, Shimakawa Y and Kubo Y 2005 J. Phys. Soc. Japan 74 970
[11] Basov DN and Timusk T 2005 Rev. Mod. Phys. 77 721
[12] Ikemoto Y, Moriwaki T, Hirone T, Kimura S, Shinoda K, Matsunami M, Nagai N, Nanba T, Kobayashi K, Kimura H 2004 Infrared Phys. Tech. 45 369
[13] Moriwaki T and Ikemoto Y 2008 Infrared Phys. Tech. 51 400
[14] Fukazawa H, Hirayama K, Yamazaki K, Kohori Y and Matsumoto T 2007 J. Phys. Soc. Japan 76 125001
[15] Uwamoto Y 2007, in Handbook of High Pressure Technology, ed Mohri N, Murata K, Uwamoto Y and Takahashi H (Tokyo: Maruzen)
[16] Fukui K, Miura H, Nakagawa H, Shimoyama I, Nakagawa K, Okamura H, Nanba T, Hasumoto M and Kinoshita T 2001 Nucl. Instr. Methods Phys. Res. A 467-468 601
[17] Dressel M and Gruner G 2002 Electrodynamics of Solids (Cambridge University Press, England)
[18] Matsunami M, Okamura H, Ochiai A and Nanba T 2009 Pressure tuning of an ionic insulator into a heavy electron metal Preprint arXiv:0907.4545v1
[19] Syassen K, Winsen H, Zimmer HG, Tups H and Leger JM 1985 Phys. Rev. B 32 8246
[20] Syassen K 1986 Physica B+C 139-140 277