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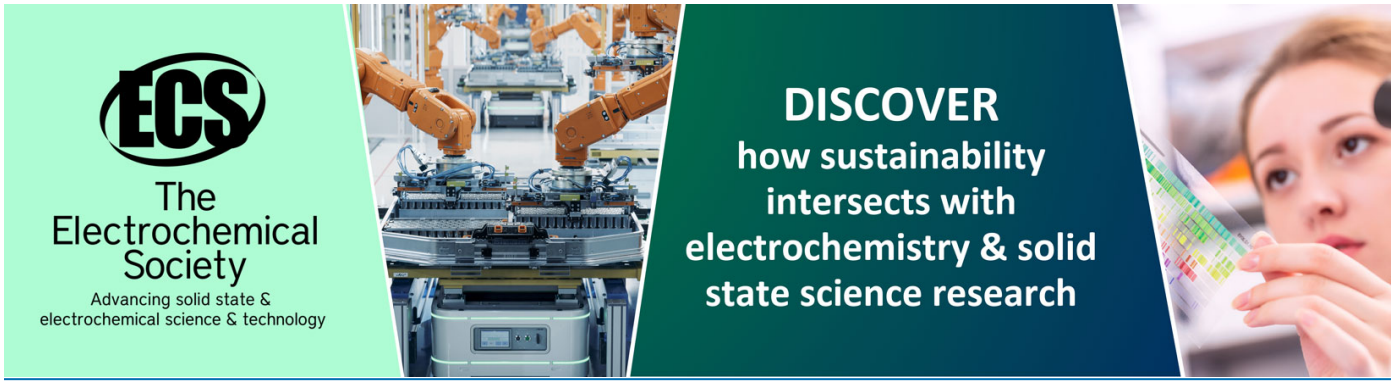

Journal of Physics: Conference Series **150** (2009) 042070 doi:10.1088/1742-6596/150/4/042070

Observation of charge ordering state in LiV_2O_4 investigated by optical study

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Abstract. We have been investigated the electronic states of LiV_2O_4 under high pressures and low temperatures analyzed by optical study using an infrared microscope. The optical conductivities derived from reflectivities clearly exhibit the change from a metallic state at ambient pressure to an insulating state at 13 GPa with the pseudo gap of $\Delta \sim 0.5$ eV at the low temperature of 40 K. The Drude response observed at ambient pressure declines at high pressures even at 300 K. A softening phenomenon of a residual ray band structure is verified through the temperature change from 300 K to 40 K at 13 GPa.

1. Introduction

LiV_2O_4 has been found to show a heavy fermion state for the first time in $3d$ metal oxides. The large coefficient $A = 2.0$ $\mu\Omega$ cm/K^2 of the T^2 term in electrical resistivity and the large $\gamma \sim 350$ mJ/mol$\cdot$ K^2 obey the Kadowaki-Woods relation [1]. The crystal remains cubic spinel structure above 9 K [2] and the long-range magnetic order is absent down to 20 mK in spite of the short-range correlation below 20 K [3, 4]. Vanadium in LiV_2O_4 has a half integer valence number of +3.5 ($d^{1.5}$) on the average and should be exhibit the alternated valence numbers of V^{3+}:V^{4+}=1:1 or V^{3+}:V^{5+}=3:1 in an insulating state. Under hydrostatic pressure, the low temperature metallic state drastically changes to an insulating state [5, 6]. A formation of charge ordering has been predicted in this pressure-induced insulating state. The structural distortion involving the distribution of V-V bond length is confirmed by a x-ray diffraction analysis and an EXAFS experiment [7, 8].

In this paper, we report the result of optical study on single crystal LiV_2O_4 under high pressures and low temperatures using infrared microscope. A pressure-induced metal-insulator transition (MIT) was observed at the low temperature of 40 K, and a pseudo gap opening was also observed at 300 K under the high pressure of 13 GPa. The phonon softening was found for a residual ray band observed at far-infrared (FIR: ~ 0.1 eV) region which stood out in the pressure-induced insulator phase.

2. Experiments

The measurements of optical reflectivity under high pressures at low temperatures were carried out for LiV_2O_4 using infrared spectromicroscopes at BL43IR of the SPring-8 and at our laboratory. The high pressures up to 13 GPa were generated using a diamond anvil cell (DAC). The achieved pressures were determined by the conventional ruby fluorescence technique [9]. The reflectivity measurements were performed on the mirror surface of the fractured single crystals. The reliable reflectivity for the sample in DAC was obtained by the multistep compensation using Au foil and evaporated Au references [10]. The optical conductivity σ was derived from the reflectivity by the Kramers-Kronig transformation.

3. Results and Discussion

Fig. 1 shows the pressure change of the reflectivity and the optical conductivity for both 40 and 300 K. As for the ambient pressure, the optical conductivities showing finite Drude responses at 40 and 300 K represent the metallic states which is consistent with the former experiment [11]. Once under high pressure, the spectra are drastically changed from that at ambient pressure. The Drude responses decline in the wide range up to 1 eV at 40 K and up to 0.4 eV at 300 K. The hump structure newly appeared in the mid-infrared (MIR: $0.1 \sim 1$ eV) region, around 1 eV for 40 K and 0.5 eV for 300 K, reflects the interband transition of the gap developing in the electronic states under pressure. At the same time, a residual ray band structure appears in the FIR region for both 40 and 300 K. The detailed spectral change by pressure is displayed in the left side of Fig. 2. The reflectivity at 40 K starts to decrease above 5 GPa. The gradual change is continued up to 11 GPa. This consecutive metal-insulator (M-I) change is consistent to the results of resistivity measurements under pressures [5, 6]. One of the possible explanations is that the short-range charge-distribution starts around 5 GPa and grows into the long-range charge-ordering at 11 GPa. The peak broadening before splitting observed in the x-ray diffraction experiment at 10 K can be derived from this short-range distribution [7]. We also focused on the change of the residual ray band structure through this gradual phase transition. Although a crystal usually becomes harder with decreasing temperature, certain phonon modes associated with a structural phase transition exhibit a softening phenomenon as a process of the mode freezing. Thus the shift of the residual ray band toward lower energy side from 300 to 40 K shown in the right hand of Fig. 2 explains the existence of structural change under high pressure in this compound. Meanwhile, the residual ray band structure never split within the realm of energy resolution of 0.5 meV in this experiment. The broad peak structure in the FIR region so called residual ray band has been explained as a result of developing a large electric dipole moment. In this compound, the formation of the charge alternation in vanadium can achieve the dielectric polarization with an insulating state. The spectral features under high pressure, i.e., the formation of the new gap structure and the softening phenomenon in the residual ray band, are consistent with the formation of a charge ordering state including a slight structural distortion through the M-I transition.

4. Acknowledgments

This work was partly supported by Grant-in-Aid for Scientific Research (No. 19560665) from MEXT, Japan. A part of this work was performed as a Joint Studies Program of the Institute for Molecular Science (2007) and was done using the infrared microspectroscopy apparatus at BL43IR of the SPring-8 (Proposal Nos. 2006B1406, 2007A1129, 2007B1101) with the approval of JASRI. We thank Dr. T. Moriwaki and Dr. Y. Ikemoto of JASRI for technical assistance.

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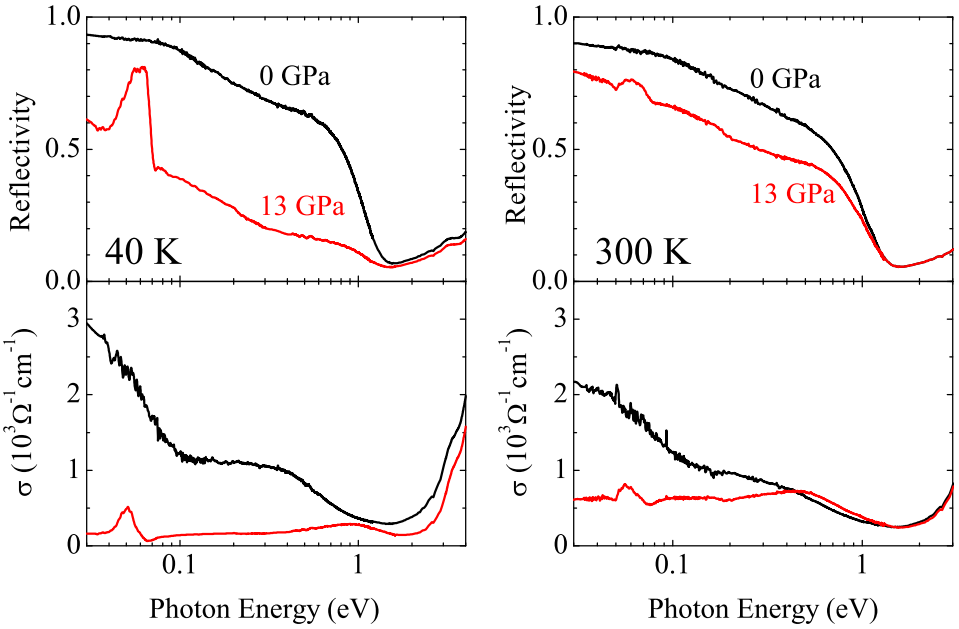

Figure 1. Optical reflectivities and conductivities at 40 and 300 K under ambient pressure and 13 GPa.

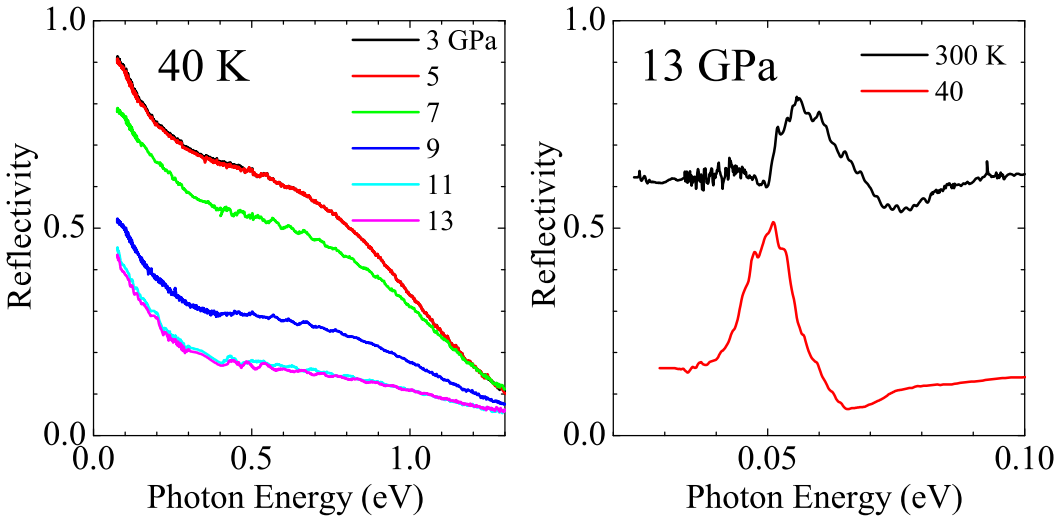

Figure 2. Pressure change of reflectivity in MIR region at 40 K (left side). The temperature change of FIR peak structure is also shown (right side).

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