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Metal-insulator transition in V_6O_{13} probed by photoemission and optical studies

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Abstract

The metal-insulator (MI) transition in quasi-one-dimensional compound V_6O_{13} has been investigated by angle-resolved photoemission spectroscopy (ARPES) at the photon energy of $h\nu$=10 eV using synchrotron radiation and optical study below 2 eV. Along the $b \parallel$ direction, a clear Fermi cutoff and a band dispersion near E_F

are observed in the ARPES spectra. The energy distribution curves (EDC) show an opening of a gap ~0.2 eV across the transition temperature T_{MI}=150 K. The ARPES at $h\nu$=10 eV is confirmed to be a bulk-sensitive spectroscopy with high resolutions in energy and momenta.

Key words: V_6O_{13}, Wadsley phase, ARPES, optical conductivity

PACS: 71.10.Pm, 71.20.-b, 71.30.+h, 78.30.-j, 79.60.-i

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1 Introduction

There have been many studies for vanadium oxides. Among them, mixed-valence compounds of Magnéli phase (V_nO_{2n-1}) and Wadsley phase ($V_{2n}O_{5n-2}$) show complicated physical properties, such as MI transitions accompanied by magnetic transitions [1,2]. V_6O_{13} belongs to the Wadsley phase. Despite the great interest, there have been limited numbers of studies because of the complicated physical properties and the crystal structure in contrast to the well-known V_2O_3. V_6O_{13} shows a MI transition at T_{MI}=150 K and an antiferromagnetic transition at T_N=55 K [7–12]. In its crystal structure, there are two different types of one-dimensional vanadium networks along the b-axis [3–6]. Several different vanadium valence numbers are thought to exist in both metallic and insulating phases [12]. In order to investigate the change of electronic structure near the Fermi level through the MI transition, we have performed a low-energy ARPES and an optical study with polarized light sources.

2 Experimental

ARPES experiment was carried out by using synchrotron radiation at BL9A in HiSOR with a Scienta SES2002 analyzer. The excitation photon energy was selected as $h\nu$=10.05 eV for bulk-sensitive measurements. The energy and angular resolutions were set to be better than 100 meV and $\pm 0.5°$. The ARPES measurements were done at 110 and 170 K, below and above T_{MI}. Clean surfaces for the bulk-sensitive measurements were obtained by cleaving the single crystal samples in situ under an ultra-high vacuum of better than 2×10^{-8} Pa. The crystal directions were certified by X-ray Laue diffraction method in advance to the measurements.

Optical reflectivity measurements were performed using a Fourier interferometer and conventional light sources up to $h\nu$ $\leq$1.8 eV. Flat sample surfaces were obtained by cleaving single crystals in the (110) face. Gold was deposited on the samples after the measurements as a reference for deriving accurate reflectivity. Optical conductivity σ was obtained from the optical reflectivity by using the Kramers-Kronig relation [13]. For the proper K-K transformation, the optical reflectivity spectra were complemented on the lower energy side by Hagen-Rubens and a constant extrapolations for the metallic and insulating phases, respectively. As usual, ω^{-4} extrapolation was employed on the higher energy side in this study.

3 Results and Discussion

Figure 1 shows the intensity maps made of EDCs and the momentum distribution curves (MDC) for b $\|$ direction at 170 and 110 K. At 170 K, a small

upward dispersion is seen around kb/π=0 in the intensity map. The upward band dispersion crosses E_F at $kb/\pi \sim 0.4$. In contrast, there is no intensity at E_F and angular dependence is negligible near E_F at 110 K. No significant dispersion is seen in MDC.

The spectral changes of EDCs across T_{MI} for $b \parallel$ direction are shown in Figure 2 for several angles. The MI transition is clearly seen as a change near E_F with opening a gap of ~0.2 eV. At 170 K, a finite intensity exists at E_F in every EDC contrary to the former study performed with using a He discharging lamp [14]. The spectral intensities at $0 \sim 0.3$ eV seem to transfer to $0.7 \sim 2.1$ eV regions with the change from the metal to the insulator phase. The gap formation and spectral change resemble the higher-energy photoemission results [15]. The details of the band structure above 2 eV are hidden by secondary electron backgrounds. According to the cross-sections, the difference from high-energy ARPES may be resulting from the O 2p sensitivity in low-energy ARPES compared with the V 3d sensitivity in high-energy ARPES [16].

Figure 3(a) shows the optical reflectivity. For the metallic phase at 300 K, thick and thin continuous lines correspond to the spectra measured for the polarization along the b- and a-axes as parallel and perpendicular to the vanadium networks. Similarly, thick and thin dashed lines are in the semiconducting phase. The spectra change discontinuously at T_{MI} with changing temperature and the typical spectra for metallic and semiconducting phases are given in the figure. In Figure 3(b) are shown the optical conductivity spectra that are obtained from the reflectivity spectra of 0~3 eV region extended by the extrapolations as mentioned before. Both in the reflectivity and the conductivity, the intensity difference at $h\nu$=0 eV and the energy range with spectral

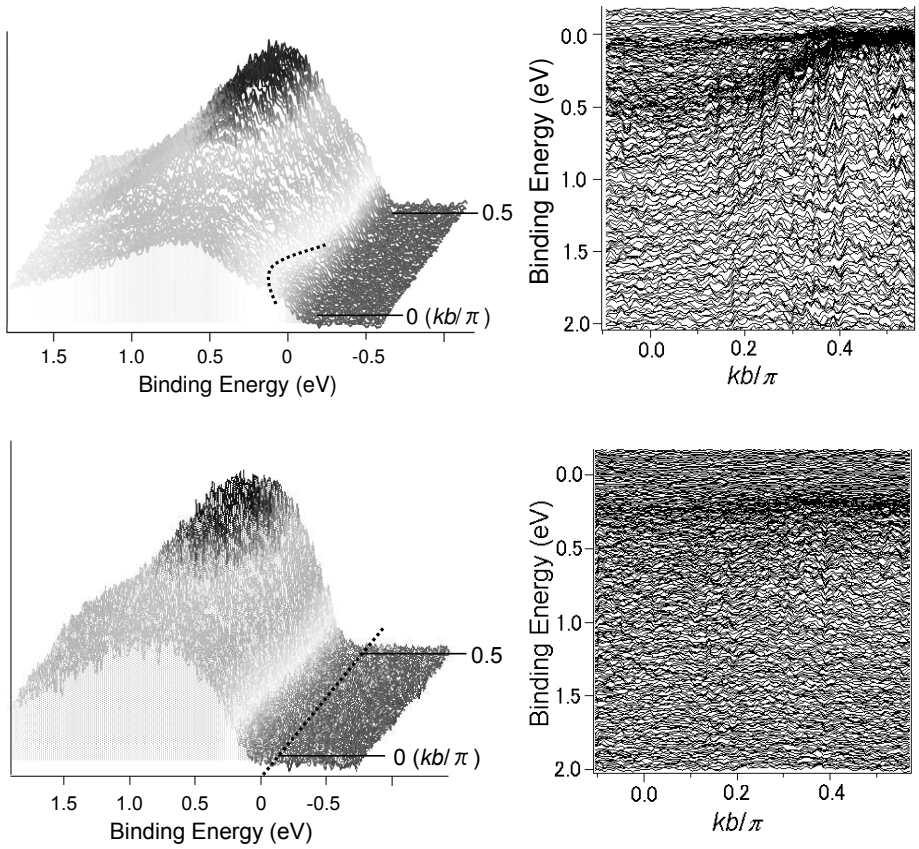

Fig. 1. Intensity maps and MDCs in $b \parallel$ direction at 170 and 110 K.

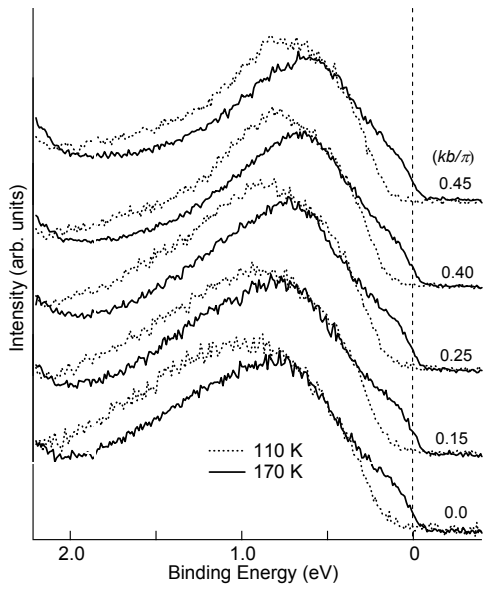

Fig. 2. Changes in EDCs at several angles across the MI transition temperature.

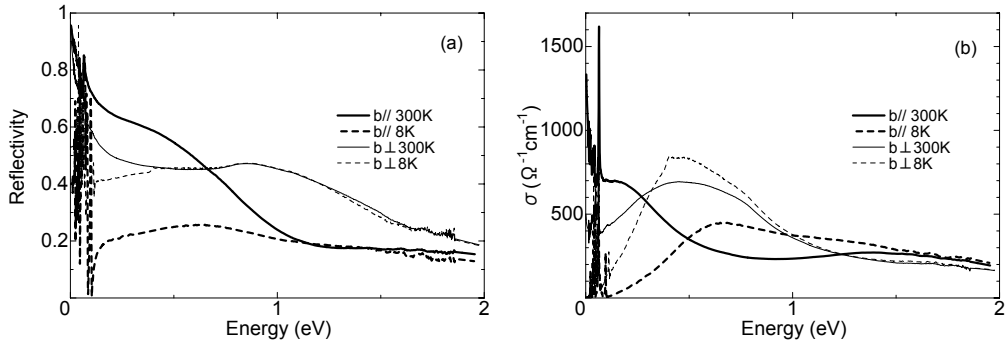

Fig. 3. Spectral changes in optical reflectivity and conductivity across the MI transition temperature.

change across T_{MI} are larger for $b \parallel$ than in $b \perp$ direction. The discrepancy in conductivity is observed below $\sim$ 1.6 eV in $b \parallel$ and below $\sim$ 1.2 eV in $b \perp$. Especially in $b \parallel$ conductivity the smallest band gap from the occupied to unoccupied states is opened as $\sim$ 0.3 eV. The spectral intensity of Drude weight in the metallic phase seems to transfer to the hump at $\sim$ 0.6 eV. It may correspond to the relocation of spectral weight across T_{MI} observed in the EDCs namely the opening the Mott gap in the insulator phase. Extensive analysis requires the measurement up to higher photon energies with using synchrotron radiation light sources [17].

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