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Electronic structure of VO₂ near phase transition by tunnelling spectroscopy

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Abstract

Tunnelling spectroscopy has been performed on W-doped VO₂ single crystal near the metal–insulator transition temperature. A remarkable change was observed in the electronic density of states of the conduction band just below the transition temperature. Based on the observed results, a model is proposed for the onset of the metal–insulator transition in VO₂ in relation to the band diagram by the local density approximation plus Hubbard U calculation. The tunnelling energy gap observed was in good agreement with band calculations and optical measurements near the transition temperature.

1. Introduction

Vanadium dioxide (VO₂) undergoes a metal–insulator transition (MIT) at about 340 K, which is a first-order phase transition accompanied by a structural change from a high-temperature rutile type to a low-temperature monoclinic type [1, 2]. Dramatic changes of VO₂ in electrical resistivity and infrared transmission have attracted physical interest and attention for temperature sensing devices, optical switching devices, optical data storage media etc over a long time [3]. Recently, an electric field effect in correlated oxide materials has attracted much attention, because of the possibility of applications to new electronic devices such as the Mott-transition field-effect transistor (MTFET) which is a candidate substitute for the silicon-based FET [4–8]. The discovery of the high- T_c cuprate superconductors has also attracted renewed physical interest in the MIT in 3d transition-metal compounds [9].

The early qualitative aspects of the electronic structure in the low-temperature phase of VO₂ were explained long ago by Goodenough [2]. The d levels of the V atoms are split into a lower-lying t_{2g} state and a higher-lying e_g state because of the O octahedral crystal field. The tetragonal crystal field further splits the multiple t_{2g} state into $d_{||}$ and π^* states. There are two structural components to the lattice distortion in the low-temperature phase, namely a pairing

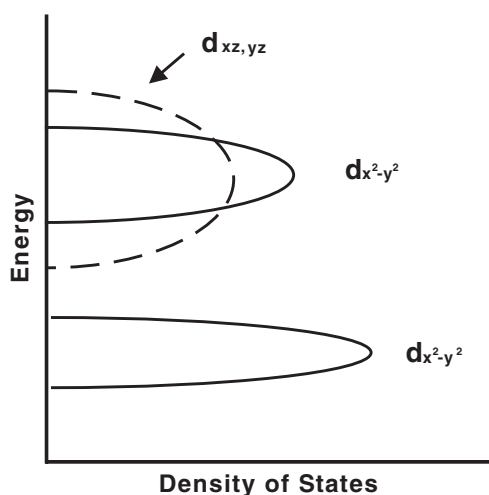


Figure 1. Schematic illustration of VO₂ bands in the monoclinic structure. The upper and lower $d_{x^2-y^2}$ bands are Mott–Hubbard split bands. The band gap exists between the bottom of the $d_{xz,yz}$ band and the top of the lower $d_{x^2-y^2}$ band. The energy scale is arbitrary.

and a twisting of V atoms out of the rutile axis c_r . The pairing and twisting of the V atoms result in two effects on the electronic structure. First, the π^* band is pushed higher in energy, due to the tilting of the pairs, which increases the overlap of these states with O states. Second, the $d_{||}$ band is split into a lower-energy bonding combination and a higher-energy antibonding combination. The band gap exists between the bottom of the π^* band and the top of the bonding $d_{||}$ band.

On the other hand, for such a Peierls-like band gap, Zylbersztein and Mott [10] and Rice *et al* [11] suggested that a crystallographic distortion is not sufficient to open up a gap, and that the electron-correlation effects play an important role in opening the gap. Zylbersztein and Mott also suggested that the role of the crystallographic distortion is only to provide empty π^* bands. In today's studies, although the role of the pairing and twisting of V atoms has often been the topic of debate, the MIT of VO₂ is widely regarded as a Mott–Hubbard transition [12–14]. The recent study of band calculation via local density approximation plus Hubbard U (LDA + U) has estimated the band gap to be about 0.7 eV [14]. Figure 1 shows a schematic illustration for the density of states calculated within the LDA + U method.

Experimentally, Barker *et al* suggested that the energy band gap is 0.31 eV from optical transmission measurements [15]. Using optical absorption, Ladd *et al* [16] and Merenda *et al* [17] measured 0.62 and 0.45 eV just below the transition temperature, respectively. The definitions of the band gap, derived from optical data, are different between Ladd *et al* and Merenda *et al*. Shin *et al* [18] have estimated the energy band gap to be about 0.7 eV from UPS + reflectance measurements. Zylbersztein and Mott [10] have estimated the electrical band gap to be about 0.8 eV, assuming that localized electron pairs and excited itinerant electrons occupy different d orbital states and assuming that Hund's-rule coupling together with dielectric polaron formation provides a substantial increase in effective mass in the conduction band.

Tunnelling spectroscopy is one of the most promising methods for determination of the band gap. Tunnelling studies have shown interesting results for phase transitions, such as in superconductors and transition-metal dichalcogenides and so on (e.g. [19, 20]). Recently, the electronic structures in VO₂ were reported by scanning tunnelling spectroscopy (STS) [21, 22].

However, a study of the behaviour of the change in electronic structure in the phase transition has so far not been made.

In the present study, tunnelling measurements were carried out on W-doped VO₂ as a function of temperature near the phase transition, in order to investigate the change in the electronic structure through the phase transition. Tungsten was doped lightly to reduce the electrical resistivity in the low-temperature phase, for the sake of minimizing the potential drop across the bulk of VO₂, and thus minimizing the spectroscopic error. Tungsten atom acts as a donor in VO₂. The similarity in ρ - T characteristics between the W-doped sample and nondoped VO₂ suggests that the electronic structure is not changed basically by the W doping.

2. Experiments

2.1. Crystal growth

A single crystal of VO₂ was grown by the method of Ladd *et al* [16], using VO₂ and V₂O₅ powders and with WO₃ powder for W doping. The well-mixed powders were sealed in a quartz tube of 90 mm (long) \times 10 mm (diameter) under 1×10^{-3} Pa. The sealed quartz tube was placed vertically in a furnace. The temperature of the furnace was kept at 1000 °C for 5 h and then decreased at a rate of 2.67 °C h⁻¹ to 800 °C. At 800 °C, the quartz tube was inverted in the furnace so as to separate the useless solution from the crystals grown in the melt at the bottom of the quartz tube. The crystals were annealed for 2 h at 800 °C in the inverted tube, and then the furnace heater was switched off. The typical size of the crystals obtained was $3 \times 1 \times 1$ mm³. X-ray diffraction (XRD) elucidated that the samples were VO₂ single crystals. The crystalline *c*-axis of high-temperature rutile type lies along the length of the crystal.

2.2. Tunnelling spectroscopy measurements

Tunnelling measurements were carried out using an Al/Al₂O₃/sample planar-contact structure. The Al₂O₃/Al structure was fabricated as follows. Al was evaporated onto a clean quartz substrate. Then it was heated in the evaporation chamber at \sim 100 °C for 1 h in an O₂ atmosphere of 1 atm to oxidize the Al surface. For the back electrode, the sample was bonded to a copper plate using silver paste. The Al₂O₃ surface was pressed to the sample surface using a phosphor-bronze ribbon spring to form a stable contact tunnel junction, as shown in figure 2. Using this planar-contact method, the tunnel junction resistance can be adjusted by controlling the pressure from the top of the apparatus through a rotating shaft with a fine-pitch screw. To avoid the influence of the series resistance of the lead wire on tunnelling spectroscopy, a quasi four-probe method was employed in measuring the bias voltage V . The valence and conduction bands lie in the negative and positive bias regions, respectively. Tunnelling spectroscopy was performed using the ac modulation technique. The modulation bias and frequency were 1 mV and 1 kHz, respectively.

In this study, the planar-contact structure, as shown in figure 2, was employed as the tunnel junction, instead of the more conventional method of evaporating an insulator material onto the sample surface, because in the latter case the intimate contact, and sometimes atomic diffusion, between the insulator and the sample tends to suppress the structural change associated with the MIT near the surface of the sample.

On the other hand, a tunnel junction with the planar-contact structure is less stable and the probability that the tunnel junction is stable throughout the temperature range for all the measurements is rather low. So, it is usual that trialing several times is necessary to obtain a set of data as shown in figure 5.

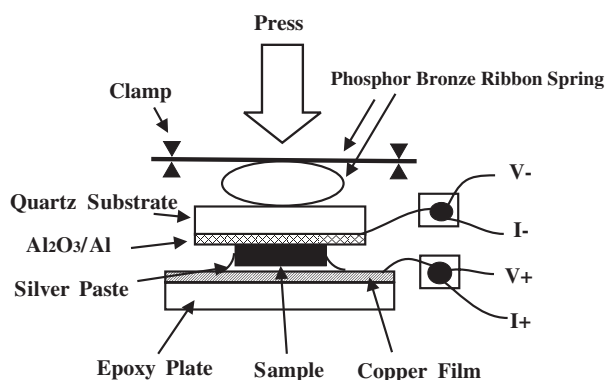


Figure 2. Schematic illustration of the tunnel unit.

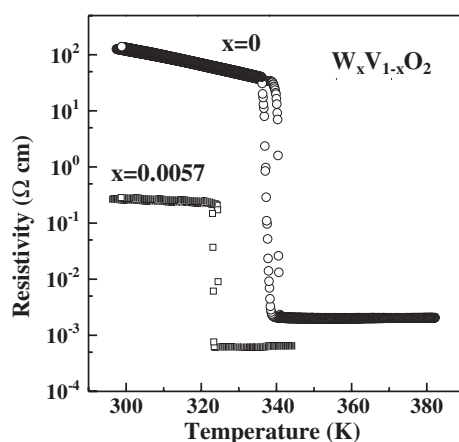


Figure 3. Temperature dependences of electrical resistivities for $W_xV_{1-x}O_2$ with $x = 0$ and 0.0057.

3. Results and discussion

In order to estimate the MIT temperature (T_i) and other parameters of the phase transition, the temperature dependences of the electrical resistivities in $W_xV_{1-x}O_2$ with $x = 0$ and 0.0057 were measured along the c -axis of rutile type by using a four-probe method. The W content was estimated using electron-probe micro-analysis (EPMA). The temperature dependences of the electrical resistivities are shown in figure 3. When the W was doped, the T_i shifted to lower temperature and the ratio of electrical resistivities on both sides of the phase transition was decreased. It is worth noticing that the width of the phase transition hysteresis also became smaller through W doping, which is different from the previous reports [23, 24]. The T_i of the metal-to-insulator transition for $x = 0.0057$ is 323.21 ± 0.4 K (transition completes in 0.8 K), as shown in figure 3.

Figure 4 shows the tunnelling dI/dV versus V characteristics in the temperature region near the MIT. Over the whole temperature range of measurements, the tunnelling junction was unchanged. As shown in figure 4, the temperature dependence of the electronic density of states is small in the band gap and band edges ($|V| < 0.4$ V) below T_i . However, the structure

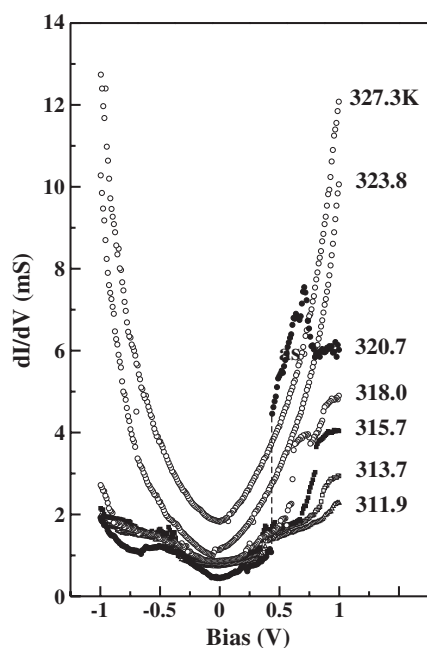


Figure 4. Temperature dependence of tunnelling spectroscopy for $W_xV_{1-x}O_2$ with $x = 0.0057$ in the temperature region around $T_t = 323$ K. Measurements were carried out from high temperature to low temperature.

changes as the temperature approaches T_t . Thus, the dI/dV versus V structure in figure 4 is not due to the surface state.

Figure 5 shows the curves shown in figure 4 shifted vertically for ease of seeing each curve. In figures 4 and 5, curves for 323.8 and 327.3 K are in the metallic state and those for 320.7 K and lower temperatures are in the insulating state. In the insulating state, an energy gap structure with diminished electronic density of states appears. The apparent residual density of states in the gap region might be due to some non-tunnelling components. For temperatures above T_t , the gap structure disappears and the curves show a metallic state.

Figure 6 shows the temperature dependence of the energy gap, estimated from the separation of biases for the maxima of $|d^2I/dV^2|$ in positive and negative biases in $|V| < 0.5$ V. The tunnelling energy gap is in good agreement with those from optical studies [16, 18].

When the temperature approaches T_t in the insulating state ($T < T_t$), a remarkable change in the density of states is seen in the positive bias region, which corresponds to the energy in the conduction band. At the measured lowest temperature, an additional increase in the density of states appears above +0.8 V. With increasing temperature, this increase in the density of states shifts toward lower bias voltage. When the front of the increase approaches the conduction band edge with increasing temperature, the band gap becomes blurred, and then the sample turns into a metallic state, which marks the T_t .

Now, we would like to consider this behaviour in the change of density of states, which seems to lead to the MIT, in relation to the band diagram in figure 1. At low temperature ($T \lesssim 315$ K), the band gaps, shown in figures 4 and 5, might correspond to the energy separation between the $d_{xz,yz}$ and the lower $d_{x^2-y^2}$ bands in figure 1. Thermal carriers are excited across the band gap and, moreover in this case by W doping, electrons are provided in the bottom of the $d_{xz,yz}$ band. As the upper band, where the electrons are provided, is not the

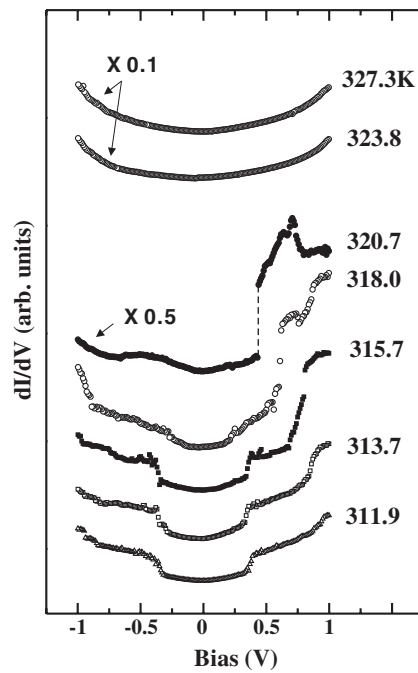


Figure 5. Temperature dependence of tunnelling spectroscopy in figure 4, shifted vertically.

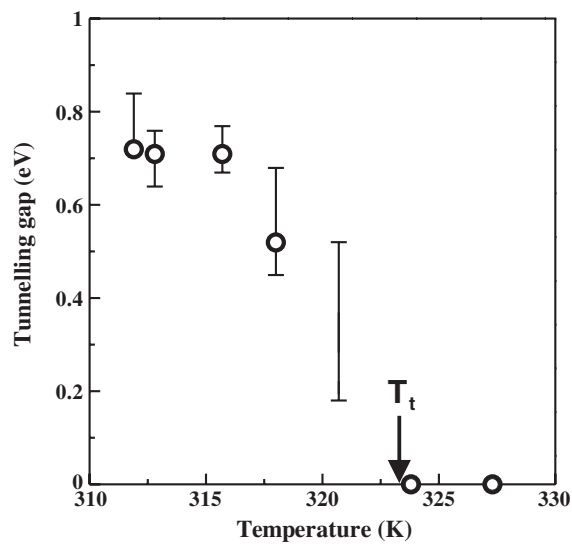


Figure 6. Temperature dependence of tunnelling energy gap in $W_xV_{1-x}O_2$ with $x = 0.0057$.

Mott–Hubbard split band (upper $d_{x^2-y^2}$ band), the effect of the carriers in depressing the gap formation is less direct compared with the case where the upper band is the Mott–Hubbard split band. Now, we might conjecture that the hump in the density of states above the bottom of the upper band is the Mott–Hubbard split band (upper $d_{x^2-y^2}$ band). This hump shifts to lower bias with increasing temperature, as shown in figure 5. When the front of the hump (bottom of the

upper $d_{x^2-y^2}$ band) approaches the bottom of the $d_{xz,yz}$ band, the electrons in the latter band transfer to the former, and thus the carriers begin to act on depressing the Mott–Hubbard gap, leading to the metallic state.

4. Conclusion

Behaviours have been clearly observed by tunnelling spectroscopy of the change in density of states in the conduction band, when the insulating state approaches the metal–insulator transition. A model has been proposed for the onset of the transition in relation to the band diagram using the recent local density approximation plus Hubbard U calculation. More investigations, including of the doping effect, are to be made to examine the above model in more detail.

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