

## Anomalous State Sandwiched between Fermi Liquid and Charge Ordered Mott-Insulating Phases of $\text{Ti}_4\text{O}_7$

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(Received 20 February 2009; published 8 March 2010)

The Magnéli phase  $\text{Ti}_4\text{O}_7$  exhibits two sharp jumps in resistivity with coupled structural transitions as a function of temperature at  $T_{c1} \sim 142$  K and  $T_{c2} = 154$  K. We have studied electronic structure changes across the two transitions using 7 eV laser, soft x-ray, and hard x-ray (HX) photoemission spectroscopy (PES). Ti 2p – 3d resonant PES and HX PES show a clear metallic Fermi edge and mixed valency above  $T_{c2}$ . The low temperature phase below  $T_{c1}$  shows a clear insulating gap of  $\sim 100$  meV. The intermediate phase between  $T_{c1}$  and  $T_{c2}$  indicates a pseudogap coexisting with remnant coherent states. HX PES and complementary calculations have confirmed the coherent screening in the strongly correlated intermediate phase. The results suggest the existence of a highly anomalous state sandwiched between the mixed-valent Fermi liquid and charge ordered Mott-insulating phase in  $\text{Ti}_4\text{O}_7$ .

DOI: 10.1103/PhysRevLett.104.106401

PACS numbers: 71.30.+h, 71.10.-w, 79.60.-i

$\text{Ti}_4\text{O}_7$  is a member of the homologous series  $\text{Ti}_n\text{O}_{2n-1}$  known as the Magnéli phase, and has been extensively studied over the past several decades because of its rich and puzzling properties [1–4]. It is a mixed valence compound and exhibits strong anisotropy in electronic conduction [5,6], with chain structures observed in STM results [7]. The system exhibits two first-order phase transitions in the temperature ( $T$ ) dependence of the electrical resistivity  $\rho(T)$  at  $T_{c1} \sim 142$  K and  $T_{c2} = 154$  K, while only one transition is observed in the magnetic susceptibility  $\chi(T)$  at  $T_{c2}$  [2]. In the low temperature (LT) phase below  $T_{c1}$ , it is well established that charge ordered chains of  $\text{Ti}^{3+}$  are separated from each other by  $\text{Ti}^{4+}$  chains. The  $\rho(T)$  has a negative temperature coefficient and  $\chi(T)$  almost vanishes in this phase, where the Ti 3d electrons are believed to be localized in  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  pairs, stabilized by a bipolaron formation [2,8]. In the high temperature (HT) phase above  $T_{c2}$ , there is no long-range order among the two types of Ti and the Ti valence is believed to be uniform 3.5+. The thermoelectric power and  $\rho(T)$  are metallic with Pauli-paramagnetic  $\chi(T)$  [8]. Thus, the HT transition at  $T_{c2}$  is attributed to a delocalization of the 3d electrons. Nonetheless, recent photoemission spectroscopy (PES) studies of  $\text{Ti}_4\text{O}_7$  have essentially revealed only the absence of a Fermi edge in the HT phase [9,10]. The extremely broad feature and no spectral weight at the Fermi level ( $E_F$ ) in the metallic state reflect a completely incoherent motion, which is in contradiction to early transport mea-

surements indicating a Fermi liquid state. This is a key controversial issue in this material.

Another contradiction is related to the nature of electronic states in the intervening region between  $T_{c1}$  and  $T_{c2}$ , which has been a subject of debate for several decades and its understanding is far from satisfactory. With decreasing  $T$  from the HT phase, the  $\rho(T)$  increases by 3 orders of magnitude at  $T_{c2}$  and shows a negative temperature coefficient. The  $\chi(T)$  almost vanishes at  $T_{c2}$  as in the LT phase. Previous x-ray diffraction (XRD) studies provided no direct evidence for a transition from charge localization to metal formation at  $T_{c2}$ , but anomalously large thermal factors were observed [11]. One of the most commonly accepted models for describing the LT phase is the Verwey model [12] with charge ordering of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . The intermediate temperature (IT) phase was viewed as a partially ordered bipolaron liquid state [2,8]. Very recently, a twist to this debate was provided by PES experiments [10] asserting that IT phase may be described by a soft-Coulomb gap (SCG) model [13], with localized Ti 3d states near  $E_F$ . However, the structure study shows appearance of a fivefold superstructure in the IT phase [14], which can imply the presence of long-range ordering. Clearly this result goes beyond the SCG and bipolaron liquid scenario with dynamical disorder. Therefore, no conclusive picture has emerged yet for the nature of the IT phase.

In this Letter, we critically reexamined the nature of electronic states near  $E_F$  and addressed two fundamental issues mentioned above. We employed various spectroscopies using a wide range of incident photon energies ( $h\nu = 7 \text{ eV} \sim 8 \text{ keV}$ ) such as core-level, off- and on-resonant valence band PES and x-ray absorption spectroscopy (XAS). We show that the HT state can be well described as a mixed-valent Fermi liquid. To our knowledge, this has not been demonstrated to date. We also found an anomalous electronic state: no gap, no Fermi edge, but with remnant coherent states near  $E_F$  in the IT phase. This behavior is at odds with the existing models. Furthermore, the HX PES of the Ti  $2p$  spectra leads to a novel phenomenological model for the electronic structure of  $\text{Ti}_4\text{O}_7$ , based on screening from the coherent states and mixed valency and how they change across the HT-IT and IT-LT transitions.

UV-laser excited (laser)-PES measurements were performed using a Scienta R4000 electron analyzer and an ultraviolet ( $h\nu = 6.994 \text{ eV}$ ) laser for the incident light [15]. The base pressure of the chamber was below  $\sim 5 \times 10^{-11}$  Torr throughout the measurements. The energy resolution was  $\Delta E \sim 5.0 \text{ meV}$ . Because of the low photon energy, we have checked that the laser-PES spectra reported here shows no angle-resolved effects by measuring for different polar angles so as to cover the entire first Brillouin zone. HX PES was performed using a photon energy  $h\nu = 7.93 \text{ keV}$ , at a vacuum of  $1 \times 10^{-10}$  Torr. The measurements were carried out at undulator beam line BL29XUL, SPring-8 using a Scienta R4000-10KV electron analyzer [16]. Soft x-ray (SX) PES was performed at BL17SU. The total energy resolution,  $\Delta E$  was set to  $\sim 0.2 \text{ eV}$  for both SX- and HX-PES measurements. The O  $1s$  XAS was obtained in total electron yield mode. Single crystals of  $\text{Ti}_4\text{O}_7$  were grown by the floating zone technique. In all measurements, clean sample surfaces were prepared by fracturing *in situ* and gold  $E_F$  was measured to calibrate the energy scale.

First, we present the on- and off-resonant PES spectra of the HT phase for a wide binding energy ( $E_B$ ) region in the inset of Fig. 1(a). The off-resonance spectrum with  $h\nu = 450 \text{ eV}$  shows a dominant contribution of the O  $2p$  states to valence band peak at binding energies of  $\sim 6 \text{ eV}$ , while a weak Ti  $3d$  feature was observed near  $E_F$  as in earlier studies [9,10]. On-resonance data in the HT phase has shown a strong enhancement of the Ti  $3d$  feature and a clear Fermi edge. This is because the narrow Ti  $3d$  band just below  $E_F$  is selectively magnified by tuning x-ray photon energy to the maximum of Ti  $L_3$  XAS white line ( $h\nu = 460 \text{ eV}$ ). The  $T$ -dependent resonant-PES spectra near the  $E_F$  are shown in Fig. 1(a). On decreasing  $T$ , the spectral weight at  $E_F$  has transferred to the higher binding energy region, forming a gap ( $\sim 100 \text{ meV}$ ) in the LT insulator phase. The spectral weight transfer occurs from  $E_F$  up to an energy scale of  $1 \text{ eV}$  and is indicative of a correlation driven Mott-insulating phase [17]. In the IT phase, however, the spectrum has shown neither a

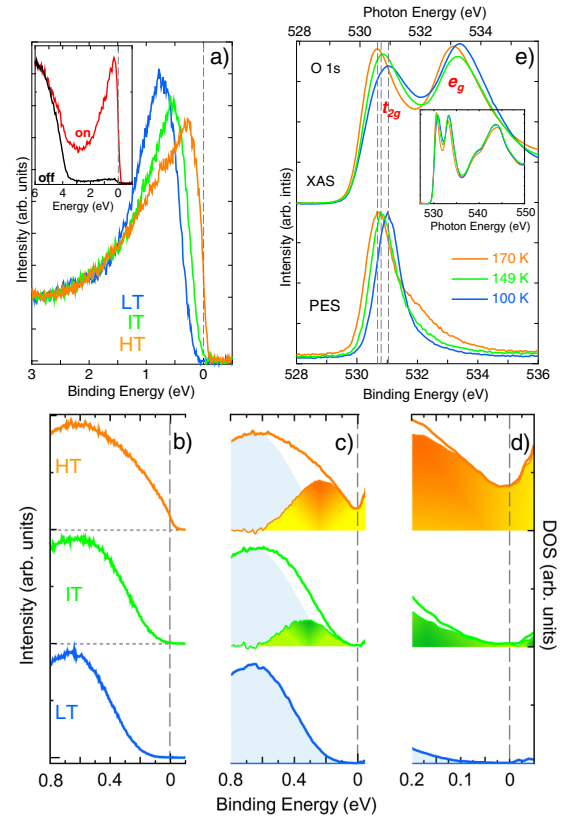


FIG. 1 (color online).  $T$ -dependent electronic structure near  $E_F$ . (a) Resonant PES at the Ti  $L_3$  edge. The inset shows the on- and off-spectra at the HT phase over a wide energy range. (b) Experimental laser-PES spectra. (c) The spectral function  $A(\omega)$ . Shaded areas (yellow and green) highlight the difference of  $A(\omega)$  to the LT-phase  $A(\omega)$  (light blue). (d) Enlarged plot of  $A(\omega)$  near  $E_F$ . (e) The O  $1s$  core-level shift of HX PES compared to XAS. Upper panel, O  $1s$  XAS. Lower panel, O  $1s$  HX PES. Wide-range O  $1s$  XAS are shown in the inset.

Fermi edge nor a real gap, and is the central issue in this Letter as discussed in the following.

To make sure whether there remains a well-defined residual spectral weight at  $E_F$  in the IT phase, we carried out laser-PES measurements with high energy resolution. The key observation here is that the IT phase spectrum showed neither a Fermi edge nor a real gap even with a high resolution of  $5 \text{ meV}$ . The  $T$ -dependent laser-PES data are shown in Fig. 1(b). The spectra have been normalized to the most intense peak in each spectrum. While the present results are seemingly similar to the results using He lamp presented previously [10], the greatly improved energy resolution in the current study allows us for the first time to finely resolve the electronic structure near  $E_F$ . Nevertheless, we could not observe any evidence of gap opening with  $5 \text{ meV}$  energy scale in IT phase. One may possibly attribute this gapless feature to the occupancy by thermally excited electrons, because of the rather high temperature ( $\sim 140 \text{ K}$ ). In order to extract the intrinsic  $T$  dependence of one electron spectral function  $A(\omega)$ , we eliminate the effect of the Fermi-Dirac function  $f(\omega)$ . We

evaluate  $A(\omega)$  by using the general expression  $I(\omega) = \int d\epsilon A(\omega - \epsilon) f(\omega - \epsilon) g(\epsilon)$ , where  $g(\epsilon)$  is the Gaussian broadening corresponding to the instrumental resolution (5.0 meV). As a results, we obtained  $A(\omega)$  not only below but also above  $E_F$  (within  $E_B \sim 5k_B T$ ), owing to the occupancy by thermal excitations. The  $T$ -dependent evolution of the extracted  $A(\omega)$  on a wider energy range ( $-0.05 \text{ eV} \leq E_B \leq 0.8 \text{ eV}$ ) and in the vicinity of the  $E_F$  are shown in Figs. 1(c) and 1(d), respectively. The yellow and green shaded areas are the difference spectra obtained by subtracting the LT phase  $A(\omega)$  from HT and IT  $A(\omega)$ , respectively. Three distinct spectral shapes were observed: (i) The LT phase has a gap of  $\sim 100 \text{ meV}$  followed by a broad peak at  $0.7 \text{ eV}$ . (ii) The presence of the Fermi edge in the HT phase is still clear although it is smaller in magnitude compared to resonance data. The smaller intensity near  $E_F$  in laser PES is due to the decrease of the photoionization cross section of Ti  $3d$  states compared to O  $2p$  states. (iii) The IT phase  $A(\omega)$  exhibited a definite but small residual spectral weight at  $E_F$ . This is the most important observation emphasized here. The pseudogap observed in the present PES spectra is similar to the suppression of the low-frequency spectral weight in optical studies [18]. This clearly shows the existence of an electronic state between  $E_F$  and  $0.6 \text{ eV}$  binding energy in IT phase. As we will discuss later, we attribute this new state to a coherent screening state.

We so far discussed on the occupied states below  $E_F$ . It is, however, important to consider that the real gap is also affected by the unoccupied state above  $E_F$ . To this end, we carried out the O  $1s$  XAS measurement, shown in upper panel of Fig. 1(e). XAS is a complementary probe of the unoccupied state of a material, providing site and symmetry projected density of states. The O  $1s$  XAS spectra exhibit a double-peaked sharp structure between  $529$  and  $536 \text{ eV}$  and a broader structure around  $536$ – $550 \text{ eV}$  [9]. The data presented here are very similar to that reported earlier [9]. The double-peaked structure has been identified to O  $2p$  states, which are strongly hybridized with unoccupied Ti  $3d$   $t_{2g}$  and  $e_g$  orbitals.

A systematic shift of the  $t_{2g}$  preedge peak at  $\sim 531 \text{ eV}$  was clearly observed as a function of  $T$ . This  $t_{2g}$  peak in the IT (LT) phase has exhibited a shift of  $100 \text{ meV}$  ( $300 \text{ meV}$ ) in peak position towards higher energy with respect to HT spectrum, while the  $100 \text{ meV}$  shift in IT phase was missing in earlier result [9]. We would like to emphasize the importance of this observation. These shifts directly indicate that the lowest energy state of the unoccupied state for the IT and LT phases are  $100$  and  $300 \text{ meV}$  higher in energy than that of the HT phase from the O  $1s$  level, respectively (see Fig. 2). On the other hand, a same amount of the peak shifts were also observed in O  $1s$  core-level HX PES [see Fig. 1(e)] which reflect the  $E_F$  shifts with respect to the O  $1s$  level, as shown in Fig. 2. Therefore, we can definitively conclude that the  $E_F$  always resides near the bottom of the conduction band, resulting in no gap above  $E_F$  for all

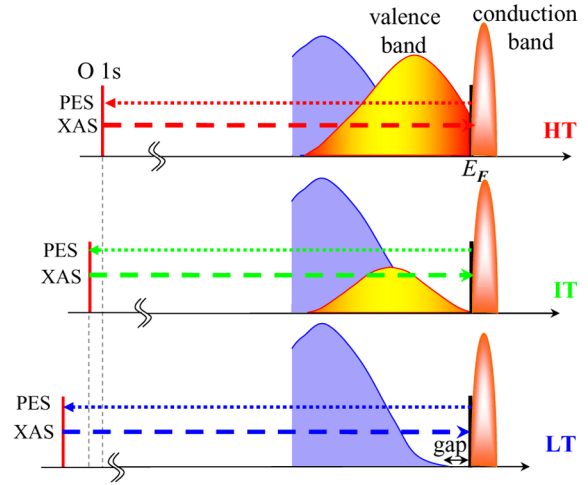


FIG. 2 (color online). Schematic pictures illustrating the evolution of the low energy electronic structure with temperature.

three phases. This conclusion is consistent with the previous study on the Seebeck coefficient  $S$  indicating that the mobile carrier is  $n$  type [8].

Further information on the nature of the pseudogap state in IT phase can be obtained from the bulk sensitive HX PES. This technique has enabled us to obtain clear evidence of the coherent screening (well-screening) due to electronic states at and near  $E_F$ . The combination with extended configuration interaction model (CIM) calculation can provide the clear evidence of the modulation of the bulk electronic state near  $E_F$  [19–22]. Figure 3 shows a complementary set of experimental and calculated Ti  $2p$  core-level spectra for the three phases. The experimental spectra in Fig. 3(a) were normalized for area under the curve. An extremely unusual  $T$  dependence was observed with clear changes across  $T_{c1}$  and  $T_{c2}$ . In the following we analyze the spectral changes in detail.

The Ti  $2p$  HX PES spectra were calculated within the extended CIM with  $C_{3v}$  local symmetry. This model is well-established and was successfully used to study the PES spectra for various materials. Details of the model have been described in previous work [19–22]. We used, as basis states, six configurations:  $3d^0$ ,  $3d^1\bar{L}$ ,  $3d^2\bar{L}^2$ ,  $3d^1\bar{C}$ ,  $3d^2\bar{C}^2$ , and  $3d^2\bar{C}\bar{L}$ . The  $3d^1\bar{C}$  represents the charge transfer (CT) between Ti  $3d$  and the coherent state at  $E_F$ , labeled  $C$ . An effective coupling parameter  $V^*$ , for describing the interaction strength between the Ti  $3d$  and coherent state is introduced, analogous to the Ti $3d$ -O $2p$  hybridization  $V$ . The parameter values used are (in eV): on-site Coulomb repulsion  $U = 4.5$ , the attractive core-hole potential  $U_c = 5.5$ , the CT energy  $\Delta = 5.0$ , the crystal field  $10Dq = 0.7$ , the trigonal crystal field  $\Delta_{trg} = -0.05$ ,  $V(e_g) = 2.9$ . The reduction factors of  $V$  are  $R_c = 0.8$ ,  $R_v = 0.9$ . Theory has reproduced the experiments very satisfactorily for all phases, as shown in Figs. 3(b)–3(d).

For a finer comparison between theory and experiment, let us first consider the sharp peak labeled  $\alpha$  of the HT phase in Fig. 3(b), where the final state is the well-screened



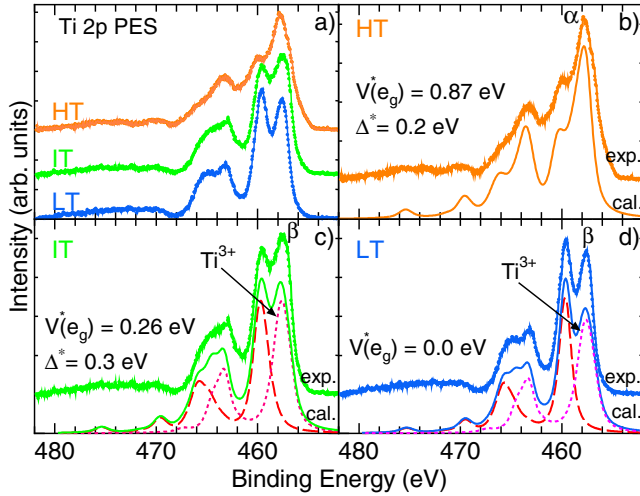


FIG. 3 (color online). (a) Comparison between experimental Ti 2p HX PES spectra for the HT, IT, and LT phases. (b),(c), (d) CIM calculations (lower panel) are compared with experiments. The dotted curves are the  $\text{Ti}^{3+}$  component.

$2p3d^1\bar{C}$  state. The screening effect from the coherent state  $\bar{C}$  near  $E_F$  leads to the formation of the low energy peak  $\alpha$ . In addition, the ground state of the HT phase mainly consists of 35.4%  $3d^0$ , 32.6%  $3d^1\bar{L}$ , and 15.4%  $3d^1\bar{C}$ , indicating a strong mixed-valent ground state. Next, we consider the LT-phase spectrum. Because of the complete absence of the coherent state near  $E_F$  in LT insulating phase [see Fig. 1(c)], we set  $V^*(e_g) = 0$ , leading to a complete suppression of the  $\alpha$  feature. The corresponding spectrum is shown by dashed line in Fig. 3(d). The calculated spectrum does not account for the lowest binding energy feature, labeled  $\beta$ , which occurred 0.2 eV below the  $\alpha$  feature. The difference matches rather well with the calculated spectrum for  $\text{Ti}^{3+}$ , shown by dotted line in Fig. 3(d). This confirms the existence of  $\text{Ti}^{3+}$  in the LT phase, as is well established from various XRD studies. The total calculated spectrum is obtained by a linear combination of CIM and  $\text{Ti}^{3+}$  states with a relative weight of 50% and 50%, respectively. The agreement is remarkable [see Fig. 3(d)]. Our calculations basically confirmed the standard valence assignment: the mean valence for Ti is approximately 3.5 in the HT phase, and clear spectral signatures of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  in the LT-phase.

Finally, we discuss the IT spectrum. Since XRD studies suggest the existence of  $\text{Ti}^{3+}$  in the IT phase as well as the LT phase, the peak  $\beta$  is predominantly due to the  $\text{Ti}^{3+}$  derived state. However, there is a definite enhancement of the peak  $\beta$  compared to the LT spectrum. We attribute this enhancement to the screening from the small amount of the coherent state, as shown in the shaded areas in the middle panel of Fig. 1(c). In fact, good agreement is obtained between the experiment and the calculation with the small  $V^*(e_g)$  spectra [see Fig. 3(c)]. We therefore conclude that the electronic state within the gap in IT phase has a

coherent character. The present results together with the previous superstructure observation suggest that the interpretation beyond the bipolaron liquid and SCG picture is necessary in the IT phase.

In conclusion, we have investigated the evolution of the electronic structure of  $\text{Ti}_4\text{O}_7$  with temperature by using the various spectroscopy and addressed two important issues. Figure 2 summarizes our main results. From O 1s XAS and HX PES, the existence of a gap above  $E_F$  was not observed. Thanks to the sensitivity of resonant PES to the Ti 3d state, the Fermi edge was observed clearly in HT metal phase, suggesting the Fermi liquid phase. In the intervening region between the HT Fermi liquid and LT charge ordered phases, the pseudogap feature (no-gap, no-Fermi edge) was observed in laser PES. Contrary to the SCG model, Ti 2p HX PES results have indicated that this pseudogap feature is associated with the coherent screening states.

M. T. would like to thank A. Fujimori for useful information and discussions. This experiment with soft x ray was carried out with the approval of the RIKEN SPring-8 Center (Proposal No. 20080054). This work was partially supported by KAKENHI (20540324).

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