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Infrared reflectance and photoemission spectroscopy studies across the phase transition boundary in thin film vanadium dioxide

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Abstract

Optical properties and valence band density of states near the Fermi level of high-quality VO_2 thin films have been investigated by mid-infrared reflectometry and hard-UV ($h\nu = 150$ eV) photoemission spectroscopy. An exceptionally large change in reflectance from 2 to 94% is found upon the thermally driven metal–insulator transition (MIT). The infrared dispersion spectra of the reflectance across the MIT are presented and evidence for the percolative nature of the MIT is pointed out. The discrepancy between the MIT temperatures defined from the electrical and optical properties is found and its origin is discussed. The manifestation of the MIT is observed in the photoemission spectra of the V 3d levels. The analysis of the changes of the V 3d density of states is done and the top valence band shift upon the MIT is measured to be 0.6 eV.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The phenomenon of the metal–insulator phase transition in strongly correlated electron systems is one of the focus areas of research in condensed matter physics [1]. The interest is partly motivated by the potential of the materials exhibiting a metal–insulator transition to be used in novel electronics and electro-optic applications as switches or memory elements [2–5]. There is also considerable interest in understanding the fundamental science behind the correlated electron behavior responsible for the striking material property changes such as the metal–insulator transition and colossal magnetoresistance. Vanadium dioxide has received special attention because of the substantial scale of the metal–insulator transition (MIT) in this material, the fact that the transition temperature is near room temperature (∼67 °C) and extremely fast optical switching upon the transition (∼100 fs) [6].

In this paper, we study vanadium dioxide thin films exhibiting a four orders of magnitude change in electrical resistance at the metal–insulator transition. We investigate how the MIT is manifested in optical properties. Specifically, optical reflectance at various temperatures is studied in the photon energy (PE) range PE = 0.1–1.05 eV. The reflectance spectrum at PE > 1 eV is affected by inelastic scattering involving interband transitions [7, 8]. We characterize these phenomena using photoemission spectroscopy of the valence bands below and near the Fermi level (0–35 eV). The novelty and significance of our work is that we present the energy dispersion spectra of optical reflectance that strongly changes upon the MIT and we observe evidence of the percolative nature of the phase transition in the reflectance data. In addition, an analysis of changes in the density of states near the Fermi level upon the MIT and a comparison of electrical and optical parameters of the MIT are made. Our results are valuable for understanding the origin of the MIT and possibly advancing the development of novel functional devices such as optical switches, high-speed modulators and logic elements based on phase transitions.

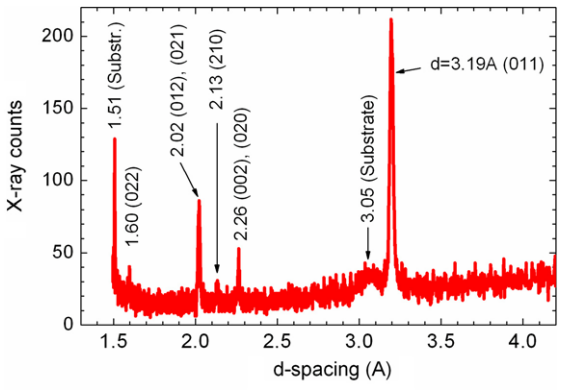

Figure 1. XRD spectrum from a VO_2 thin film on Si(001)/SiO_2 (native oxide) substrate. d values (in Å) of the peaks are inscribed and for VO_2 lines corresponding Miller indices of the Bragg planes are given in brackets according to [12].

2. Experimental details

Vanadium dioxide thin (∼100 nm thick) films were reactively DC sputtered in a Ar(91.2%) + O_2(8.8%) environment at 10 mTorr from a V target. The base pressure in the sputtering chamber was 2×10^{-8} Torr. The substrate was kept at 550 °C during the deposition. The amount of Ar and O_2 in the sputtering chamber was carefully controlled by mass flow controllers. As soon as the deposition was finished the VO_2 samples were transferred to the load lock and rapidly cooled down to room temperature using an atmospheric pressure N_2 environment to minimize post-deposition annealing. The latter step considerably improved the magnitude of the metal–insulator transition in comparison to the synthesis procedure where the samples were left in the sputtering chamber to slowly cool down in vacuum [9]. Electron transport and infrared reflectance measurements were performed on VO_2 films on c-plane Al_2O_3 substrates, while films on Si(001) substrates were used for the x-ray diffraction and photoemission studies.

The electrical resistance measurements were performed in an environmental probe station. A sample was placed on a thermal table and precision electrical probes were brought into contact with the sample surface. The resistance measurements were performed on unpatterned films with a probe separation of approximately 3 mm. Each resistance data point was calculated from the measurement of the current versus voltage curve. The linearity of the curve was checked to ensure that there were no Joule heating effects. Our earlier reported experiments confirmed the agreement between the electrical measurements on unpatterned films described above and on VO_2 lithographically patterned into microdevices [10].

Measurements of the spectral reflectance of the VO_2 film on sapphire were performed with a Perkin-Elmer Spectrum GX Fourier-transform infrared spectrophotometer. A fixed-angle reflectance attachment with a 5 mm diameter aperture was used in order to perform the measurement. The angle of incidence from the substrate normal was fixed at 16°. The x-ray diffraction measurements were done on a Scintag 2000 diffractometer using Cu Kα radiation in θ–2θ geometry. The photoemission spectroscopy (PES) was performed at the

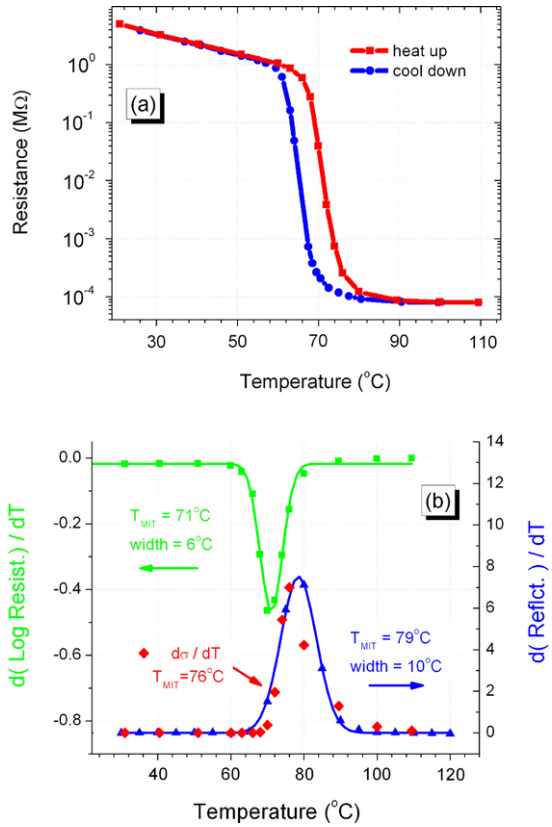

Figure 2. 100 nm thick VO_2 film on an Al_2O_3 substrate. (a) Electrical resistance, (b) green squares with a solid line connecting them—the temperature derivative of log R during heating shown in (a) and a Gaussian fit to the data; red diamonds—the derivative of the conductivity corresponding to heating data in (a) on a linear scale; blue triangles—the derivative of the reflectance of 0.13 eV photons from figure 3(b); blue line with triangles—Gaussian fit.

U12a line of the National Synchrotron Light Source at the Brookhaven National Laboratory [11]. PES angle-integrated spectra were recorded with the x-ray photons incident at an angle of 45° to the sample surface. The as-grown VO_2 film surface was studied in PES experiments with no prior mechanical or chemical treatments.

3. Results and discussion

A thin vanadium dioxide film on Si substrate was characterized by x-ray diffraction (XRD) as shown in figure 1. The d-spacing values of the observed peaks are inscribed in the figure and the VO_2 line assignment is done according to Israelsson *et al* [12]. A comparison of the measured XRD spectrum with published data [12, 13, 10] indicates high-quality polycrystalline stoichiometric VO_2.

Figure 2(a) shows the electrical resistance plot from a thin film VO_2 sample. The resistance change is over four orders of magnitude, comparable to the sharpest reported MIT in single crystals [14] and epitaxial films [15]. The point of the highest gradient of this log R curve is usually taken to define the MIT temperature, T_{MIT}. Figure 2(b) shows the derivative of the log R curve, $d(\log R)/dT$, fitted with a Gaussian. The center

and width of the Gaussian are 71 and 6 °C, respectively, and correspond to conventionally defined T_{MIT} and transition width Δ_{MIT}, respectively.

The mid-infrared reflectance spectra from a VO_2 film on the *c*-plane Al_2O_3 substrate are shown in figure 3. These optical measurements were done on the same film whose electrical transition is shown in figure 2 allowing a direct comparison between electrical and optical data. The temperature dependence of reflectance at selected incident photon energies is shown in figure 3(b). One can see a sharp increase in reflectance when the film is heated across the metal–insulator transition. Larger magnitude of the reflectance switching occurs at lower photon energies. For example, at $h\nu = 0.13$ eV ($\lambda = 9.54$ μm) the reflectance switches from 2% to 94% upon the MIT, which well exceeds the largest reported magnitudes of optical reflectance and transmittance switching in this material [16, 17, 8, 18]. One can see from figure 3(a) that most of the change in the spectra with temperature occurs within a 15 °C interval including the transition temperature. The magnitude of the switching seen in figure 3(b) is monotonically decreasing with increasing photon energy, while the transition interval remains the same ∼15 °C. The sharp slopes at the MIT and the flat portion of the curves below and above the transition are potentially valuable for developing applications such as optical switches.

An interesting feature is observed in the 0.8 eV reflectance curve in figure 3(b). There is a distinct decrease of the reflectance at the onset of the MIT near 75 °C. This feature is also seen in the spectra in figure 3(a). The 75 °C curve is lower than 70 °C in the energy interval from 0.75 up to 1 eV. It is worthwhile noting that the value of the bandgap in semiconducting (monoclinic lattice) VO_2 is ∼0.6–0.7 eV [7, 19]. The inelastic scattering involving excitations across the bandgap become possible in the $h\nu$ range 0.75–1 eV where a decrease in reflectance is observed. However, this may not directly explain the temperature dependence of the effect, i.e. its appearance right near the T_{MIT}. More likely, this phenomenon may be similar to the critical opalescence in liquid–vapor phase transitions. It has been shown that the semiconductor to metal phase transition in VO_2 occurs percolatively: first metallic puddles nucleate, then their sizes grow until the metallic phase percolates throughout the whole material [20, 16]. During the transition, there is coexistence of spatially separate metallic and insulating phases. When the wavelength of the incident radiation is comparable with the characteristic size of the metallic puddles, enhanced scattering is expected which would lead to the decline in reflection. The typical size of the metallic puddles in the middle of the transition can be estimated to be 1–2 μm [20]. Further growth of the metallic puddles results in complete merging of the metallic phase and consequently an increase of the reflectance. Enhanced scattering is then expected at $\lambda = 1$–2 μm (PE = 1.2–0.6 eV) in agreement with our observation.

Another interesting feature can be noted from a comparison of the electrical and optical MIT characteristics shown in figure 2(b). The derivative of the reflectance is fitted with a Gaussian to determine the optical transition temperature and width. If one assumes the MIT temperature to be the highest gradient point in the log of the resistance curve, then the T_{MIT} would be equal to 71 °C which is 8 °C, apart from the highest gradient point in the reflectance data, 79 °C. The maximum error between the sample temperature readings in electrical and optical experiments was determined to be less than 2 °C and cannot explain the mentioned 8 °C difference. To understand the origin of the discrepancy we have plotted in figure 2(b) the derivative of the electrical conductance $d\sigma/dT$ upon heating calculated from the data in figure 2(a) ($\sigma = 1/R$). We found that the point of highest gradient of the conductance, 76 °C, is closer to the optical transition point, 79 °C, and, more importantly, that the interval of the conductance change overlaps with the interval of the optical transition. The latter indicates that the film's optical characteristics can be better described as a direct function of conductance, or consequently the free carrier density, and the center of the reflectance transition occurs at the threshold conductance value close to the highest gradient of $\sigma(T)$.

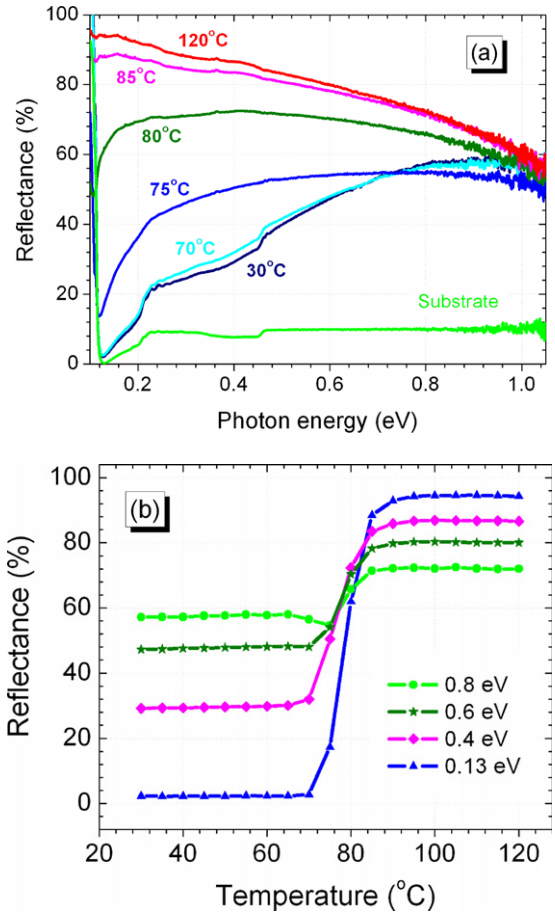

Figure 3. (a) Infrared reflectance taken from a VO_2 film as a function of incident photon energy at different temperatures; (b) reflectance change upon heating at selected photon energies.

The manifestation of the MIT in the valence band structure of VO_2 films was studied using hard-UV photoemission spectroscopy at a constant incident photon energy of 150 eV. The photoemission spectra displaying the binding energy of the valence levels below the Fermi level in the metallic and insulating states of the film are displayed in figure 4. The

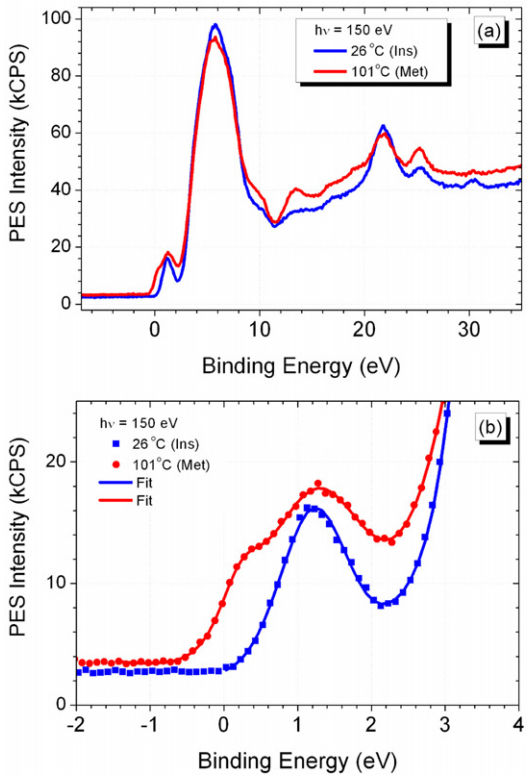

Figure 4. Photoemission results on a VO_2 thin film in the metallic (101 °C) and semiconducting state (26 °C). (a) Measured data. The positions of the peaks below the prominent O 2p peak do not change upon crossing the MIT. (b) Magnified view of the near-Fermi level structure. Symbols are measured data. Calculated fits are shown by solid lines.

metallic state was achieved by heating the sample to 101 °C. The binding energy in figure 4 was calibrated so that the spectra coincide at the most prominent peak, due to the O 2p band, which has been shown not to change in the metallic and insulating states of VO_2 [21, 22]. The coincidence of the peaks in the spectra of the metallic and insulating phases at binding energies above the O 2p peak (BE $>$ 5.7 eV) gives additional validation to the mentioned BE calibration.

Considerable electronic structure changes upon the MIT were observed in the vicinity of the Fermi level shown in figure 4(b). A clear 0.6 eV shift of the peak from the top valence band towards the Fermi level was measured. This shift is almost as large as the bandgap 0.6–0.7 eV [7, 19] which implies that the Fermi level is near the bottom of the conduction band, most likely due to the presence of oxygen defects. This situation, i.e. coincidence of the PES threshold value and the bandgap, has also been observed in V_2O_5 [23]. The presence of the defects creating donor- and acceptor-like states within the energy gap which pin the position of the Fermi level was also suggested by Berglund *et al* based on the analysis of the temperature dependence of the conductivity and activation energy in VO_2 [24]. The shift of the Fermi level towards the conduction band implies that the VO_2 semiconductor is of n-type. This is in agreement with previous studies on carrier transport in single-crystal VO_2 by Rosevear *et al* indicating the carriers to be of n-type across the transition boundary [25].

In figure 4, the peaks near 1 eV above the O 2p peak are due to the V 3d bands [26, 19, 22]. We see qualitatively the same behavior of the spectra as was reported for bulk VO_2 with photon excitation of 21 eV [21]—a peak around 1 eV present in both metallic and insulating phases and a weaker satellite appearing at the Fermi level in the metallic VO_2—with the difference that, in our data, the peaks are considerably better resolved. The latter allows us to extract the precise peak positions and widths by fitting to the measured data. The fitting was done using fitXPS software package[4]. The lineshape of each peak employed in the fitting is a numerical convolution of a Lorentzian with a Gaussian where the latter represents the broadening due to the experimental instrument function. The calculated spectra are shown in figure 4(b) by solid lines. The O 2p shoulder was taken into account as an extra peak in the fitting, so for example the metallic phase was fitted with an algebraic sum of three component peaks and a linear background. The extracted peak parameters are discussed below: the single V 3d peak in the insulating phase is located at 1.2 eV with a linewidth of 1.0 eV. In the metallic phase the doublet peak locations are 0.23 and 1.25 eV, linewidths being 0.76 and 1.5 eV.

Recent photoemission results on bulk VO_2 by Koethe *et al* showed a well-resolved V 3d structure with an unusual feature that the spectral weight was shifted mainly on the first peak (at E_F) in the metallic phase [22]. Such a spectral weight ratio agreed with the calculations by Biermann *et al* based on cluster dynamical mean field theory (CDMFT) [27, 22]. In our spectra, however, we see an opposite spectral weight ratio, i.e. the peak at E_F is at least three times less intense than the lower peak at 1.25 eV. It has been shown by Eguchi *et al* that this ratio depends on the incident photon energy [28], i.e. higher photon energies provide bulk sensitivity and the spectra demonstrate higher DOS at the Fermi level. It is thus possible that our V 3d spectra might be influenced by near-surface effects of the VO_2 film. Nevertheless, the fact that we clearly see the closure of the bandgap upon the MIT in figure 4(b) strongly suggests that the presented spectra describe the valence band structure of VO_2.

The detailed temperature dependence of the reflectance spectra presented in this paper and the noted suppression of the reflectance at the onset of the MIT may help in understanding the mechanisms governing the phase transition in vanadium oxide. Since the mechanisms governing the MIT in VO_2 is still a subject of debate [6, 29], new theoretical models attempting to accurately capture the physics of the MIT are emerging. The ability of a model to correctly describe the experimental photoemission data of the near-Fermi levels is a decisive criterion of the validity of the theoretical approach [30, 22]. In this light, we expect our well-resolved PES data on thin films with the numerical analysis to be of high relevance. Also, the remarkably large switching of the optical properties described above, the fact that the material is in thin film form, which can potentially be integrated into electronic and optical devices, and the relatively simple method of synthesis of our

[4] The fitXPS ver. 2.12 (http://www.sljus.lu.se/download.html) software from D Adams, University of Aarhus (Denmark), was used to analyze the XPS spectra with the Doniach–Sunjic parameter forced to be zero.

polycrystalline films (as opposed to epitaxial methods of film growth) make our results to be of potential significance for switching technologies.

4. Conclusion

A large change in the optical reflectance from ∼2 to 94% at $h\nu = 0.13$ eV has been found in VO_2 thin films upon the metal–insulator transition. The evolution of the reflectance dispersion curves across the MIT is presented. An unusual suppression of the reflectance at the onset of the MIT is observed and attributed to the percolative nature of the MIT, i.e. the coexistence of the two spatially separated phases during the transition [20]. A comparison between the electron transport and optical characteristics of the MIT is given and the discrepancy between the MIT temperature values defined from optical and electrical properties is elucidated. The manifestation of the MIT is observed in the V 3d photoemission spectra from an as-grown thin film and the parameters of the valence band structure near the Fermi level were extracted from the spectra.

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References

[1] Imada M, Fujimori A and Tokura Y 1998 *Rev. Mod. Phys.* **70** 1039
[2] Chudnovskiy F, Luryi S and Spivak B 2002 Switching device based on first-order metal–insulator transition induced by external electric field *Future Trends in Microelectronics: the Nano Millennium* ed S Luryi, J M Xu and A Zaslavsky (New York: Wiley) pp 148–55
[3] Newns D M, Misewich J A, Tsuei C C, Gupta A, Scott B A and Schrott A 1998 *Appl. Phys. Lett.* **73** 780
[4] Wang H, Yi X, Chen S and Fu X 2005 *Sensors Actuators* A **122** 108
[5] Lee M-J, Park Y, Suh D-S, Lee E-H, Seo S, Kim D-C, Jung R, Kang B-S, Ahn S-E, Lee C B, Seo D H, Cha Y-K, Yoo I-K, Kim J-S and Park B H 2007 *Adv. Mater.* **19** 3919
[6] Cavalleri A, Dekorsy T, Chong H H W, Kieffer J C and Schoenlein R W 2004 *Phys. Rev.* B **70** 161102(R)
[7] Qazilbash M M, Burch K S, Whisler D, Shrekenhamer D, Chae B G, Kim H T and Basov D N 2006 *Phys. Rev.* B **74** 205118
[8] Okazaki K, Sugai S, Muraoka Y and Hiroi Z 2006 *Phys. Rev.* B **73** 165116
[9] Ruzmetov D, Senanayake S D, Narayanamurti V and Ramanathan S 2008 *Phys. Rev.* B **77** 195442
[10] Ruzmetov D, Zawilski K T, Narayanamurti V and Ramanathan S 2007 *J. Appl. Phys.* **102** 113715
[11] Ruzmetov D, Senanayake S D and Ramanathan S 2007 *Phys. Rev.* B **75** 195102
[12] Israelsson M and Kihlborg L 1970 *Mater. Res. Bull.* **5** 19
[13] Griffiths C and Eastwood H K 1974 *J. Appl. Phys.* **45** 2201
[14] Ladd L A and Paul W 1969 *Solid State Commun.* **7** 425
[15] Jin P, Yoshimura K and Tanemura S 1997 *J. Vac. Sci. Technol.* A **15** 1113
[16] Choi H S, Ahn J S, Jung J H, Noh T W and Kim D H 1996 *Phys. Rev.* B **54** 4621
[17] Wang H, Yi X, Chen S and Fu X 2005 *Sensors Actuators* A **122** 108
[18] Soltani M, Chaker M, Haddad E and Kruzelesky R 2006 *Meas. Sci. Technol.* **17** 1052
[19] Shin S, Suga S, Taniguchi M, Fujisawa M, Kanzaki H, Fujimori A, Daimon H, Ueda Y, Kosuge K and Kachi S 1990 *Phys. Rev.* B **41** 4993
[20] Qazilbash M M, Brehm M, Chae B-G, Ho P-C, Andreev G O, Kim B-J, Yun S J, Balatsky A V, Maple M B, Keilmann F, Kim H-T and Basov D N 2007 *Science* **318** 1750
[21] Okazaki K, Wadati H, Fujimori A, Onoda M, Muraoka Y and Hiroi Z 2004 *Phys. Rev.* B **69** 165104
[22] Koethe T C *et al* 2006 *Phys. Rev. Lett.* **97** 116402
[23] Zimmermann R, Claessen R, Reinert F, Steiner P and Hufner S 1998 *J. Phys.: Condens. Matter* **10** 5697
[24] Berglund C N and Guggenheim H J 1969 *Phys. Rev.* **185** 1022
[25] Rosevear W H and Paul W 1973 *Phys. Rev.* B **7** 2109
[26] Sawatzky G A and Post D 1979 *Phys. Rev.* B **20** 1546
[27] Biermann S, Poteryaev A, Lichtenstein A I and Georges A 2005 *Phys. Rev. Lett.* **94** 026404
[28] Eguchi R *et al* 2007 *J. Electron Spectrosc. Relat. Phenom.* **156–158** 421
[29] Kim H-T, Lee Y W, Kim B-J, Chae B-G, Yun S J, Kang K-Y, Han K-J, Yee K-J and Lim Y-S 2006 *Phys. Rev. Lett.* **97** 266401
[30] Gatti M, Bruneval F, Olevano V and Reining L 2007 *Phys. Rev. Lett.* **99** 266402