METAL-INSULATOR TRANSITION OF Na_xWO_3 STUDIED BY ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY

SATYABRATA RAJ^{*,†,‡,§}, TAKAFUMI SATO[†], SEIGO SOUMA^{*}
 and TAKASHI TAKAHASHI^{*,†}

^{*}*WPI Research Center, Advanced Institute for Materials Research,
 Tohoku University, Sendai 980-8577, Japan*

[†]*Department of Physics, Tohoku University, Sendai 980-8578, Japan*

[‡]*Department of Physics, Indian Institute of Science Education and Research,
 Kolkata 700 106, India*

[§]*raj@arpes.phys.tohoku.ac.jp*

D. D. SARMA

*Solid State and Structural Chemistry Unit, Indian Institute of Science,
 Bangalore 560012, India*

PRIYA MAHADEVAN

*S. N. Bose National Centre for Basic Sciences,
 Sector 3, Salt Lake, Kolkata 700-098, India*

Received 31 August 2009

The electronic structure of sodium tungsten bronzes Na_xWO_3 is investigated by high-resolution angle-resolved photoemission spectroscopy (ARPES). The ARPES spectra measured in both insulating and metallic phases of Na_xWO_3 reveals the origin of metal-insulator transition (MIT) in sodium tungsten bronze system. It is found that in insulating Na_xWO_3 the states near the Fermi level (E_F) are localized due to the strong disorder caused by the random distribution of Na^+ ions in WO_3 lattice. Due to the presence of disorder and long-range Coulomb interaction of conduction electrons, a soft Coulomb gap arises, where the density of states vanishes exactly at E_F . In the metallic regime the states near E_F are populated and the Fermi level shifts upward rigidly with increasing electron doping (x). Volume of electron-like Fermi surface (FS) at the $\Gamma(X)$ point of the Brillouin zone gradually increases with increasing Na concentration due to W $5d$ t_{2g} band filling. A rigid shift of the Fermi energy is found to give a qualitatively good description of the Fermi surface evolution. As we move from bulk-sensitive to more surface sensitive photon energy, we found the emergence of Fermi surfaces at $X(M)$ and $M(R)$ points similar to the one at the $\Gamma(X)$ point in the metallic regime, suggesting that the reconstruction of surface was due to rotation/deformation of WO_6 octahedra.

Keywords: Photoemission spectroscopy; band structure; metal-insulator transition; tungsten bronze.

[§]Corresponding author.

Fig. 1. Schematic view of (a) phase diagram and (b) optical properties of the Na_xWO_3 with Na concentration (x).

1. Introduction

The first golden yellow crystals with metallic appearance were obtained by passing hydrogen over heated sodium tungstate by Wöler¹ in 1824. The metallic luster of the compounds led to the name tungsten bronzes. Tungsten bronzes are well-defined non-stoichiometric compounds of general formula $A_x\text{WO}_3$, where A is an alkali metal and x varies from zero to unity. These alkali tungsten-oxide (WO_3) based compounds have created tremendous interest among material physicists because of their technological implications. In recent years, WO_3 , modified by alkali ion incorporation or substoichiometry, exhibit many technologically important properties. Electrochromic WO_3 -based devices are currently developed for “smart windows” with variable throughput of visible light and solar energy, high contrast systems for passive and active information display, variable-reflectance mirrors, and variable emittance surfaces for controlled thermal emission.^{2,3} Many properties, including the electronic, optical, and transport properties, have been studied extensively in alkali tungsten bronzes, $A_x\text{WO}_3$. WO_3 doped with Na metal, thus forming Na_xWO_3 , shows very interesting optical properties⁴ and the color changes from yellowish-green to gray, blue, deep violet, red and finally to gold as x increases from zero to unity as shown in Fig. 1. The transport measurements of $A_x\text{WO}_3$ show very interesting properties. While Na_xWO_3 shows metal-insulator transition (MIT) at $x \sim 0.25$, other alkali metals like K, Rb, and Cs doped WO_3 shows metallic behavior for all compositions. The normal electrical transport properties of $(\text{K}, \text{Rb})_x\text{WO}_3$ for $x \leq 0.33$ show anomalous behavior in high temperature while those of Cs_xWO_3 do not.^{5–7} The anomalous high temperature transport properties primarily depend on the character of the metal ions. The MIT observed as a function of x in Na_xWO_3 is one of the most interesting electronic properties. A high metallic conduction is

Fig. 2. (a) Relationship between crystal structures with composition for the alkali-metal tungsten bronzes. (b) Hexagonal and (c) cubic crystal structure projected along (001) direction of the alkali tungsten bronzes. (d) Cubic crystal structure of NaWO_3 showing corner sharing WO_6 octahedra.

obtained for $x \geq 0.25$, while the system undergoes MIT with decreasing x .⁸ Hence the investigation of electronic structure of Na_xWO_3 is of great interest from both technological and fundamental perspectives.

An interesting observation of these A_xWO_3 is its change in crystal structure for different alkali metals A and for different x as shown in Fig. 2(a), which is also interesting to study from the structural evolution point of view. For $x \leq 0.33$, $(\text{K, Rb, and Cs})_x\text{WO}_3$ exists in hexagonal structure,⁹ whereas Na_xWO_3 shows various crystal structure (see Fig. 1) from monoclinic, to orthorhombic, to tetragonal, and finally to cubic structure with increasing x from zero to unity.⁸ In hexagonal alkali tungsten bronzes A_xWO_3 , the corner-bonded WO_6 octahedra form six-member rings as channel and A^+ ion occupy the central position of the channel thus forming alkali atom chain along the c -axis. The crystal structure in the plane perpendicular to the c -axis of the A_xWO_3 is shown in Fig. 2(b). The hexagonal channels have a radius of approximately 1.63 Å, and the Cs^+ , Rb^+ , and K^+ ions have radii of 1.69, 1.47, and 1.33 Å, respectively. The K^+ ion is smaller and lighter than Rb^+ or Cs^+ and thus binds less tightly with the WO_3 lattice. As the ion size decreases further (in the case of Na^+), the crystal no longer holds hexagonal structure and turned to tetragonal structure [see Fig. 2(c)] as observed in Na_xWO_3 . It

Fig. 3. (a) Rigid band model for WO_3 showing the Fermi level, E_F in between the bottom of the conduction band and the top of valence band. For NaWO_3 , the E_F is in the conduction band which is shown by the dashed lines. Possibilities of localization in Na_xWO_3 in (b) a conduction band tail, (c) a Na induced impurity band, and (d) a pseudo gap between LHB and UHB.

was observed that for $x \geq 0.5$, Na_xWO_3 is highly metallic with a perovskite-type crystal structure as shown in Fig. 2(d). For highly metallic Na_xWO_3 , Brown and Banks¹⁰ have shown that the crystal lattice parameter increases linearly with x [$a = 3.7845 + 0.0820x$ (Å)]. In the cubic structure of Na_xWO_3 , Na ions occupy the center of the cube, while the WO_6 octahedra are located at the cube corners. The octahedral crystal field of the six oxygen neighbors of the W split the W 5d bands into triply degenerate t_{2g} and doubly degenerate e_g bands (in the cubic phase; when the WO_6 octahedra are distorted, the degeneracy of these levels may be lifted further due to lowering of the symmetry). In WO_3 , the Fermi level (E_F) lies at the top of the O 2p bands, and WO_3 is a band insulator. Within a rigid band model as shown schematically in Fig. 3(a), the band structure of both WO_3 and NaWO_3 should be identical, with E_F at different energy positions. In Na_xWO_3 , the Na 3s electrons are transferred into the W 5d t_{2g} band and the system should exhibit metallic behavior for any value of x . However, for low concentration of $x \leq 0.25$, the material is insulating and the driving force of the MIT was under debate for a long time. Primarily there are three theoretical models to explain the observed MIT in Na_xWO_3 , and they are shown schematically in Figs. 3(b)–3(d). According to the Anderson localization model,¹¹ the random distribution of Na^+ ions in the

WO_3 lattice gives rise to strong disorder effects, which makes for the localization of states at conduction band tail and the system undergoes an MIT for low Na concentration. An alternative explanation for the MIT is the development of an impurity band (level)¹² induced by the Na doping, where the states become localized at low Na concentration. Another possibility of driving the MIT is the splitting of the band due to electron correlation at the chemical potential (or E_F),¹² where the localization occurs in a pseudogap region located between the separated bands. Among the various models proposed to explain the MIT in Na_xWO_3 , there was evidence however in favor of each of these possibilities.^{12–14} Hence, no conclusions have yet been made and the issue must be investigated more deeply and thoroughly.

The localization and delocalization of states associated with MIT occurs in a very narrow energy range close to E_F in Na_xWO_3 . High-resolution photoemission spectroscopy is an appropriate tool to illustrate the mechanism of MIT. Several works of electron spectroscopy have been published till now but most of the published literatures are based on angle-integrated photoemission data^{15–18} and were not able to resolve the mechanism of MIT, and they were conflicting with each other. Höchst *et al.*¹⁵ have performed angle-resolved photoemission spectroscopy (ARPES) on metallic $\text{Na}_{0.85}\text{WO}_3$ single crystal with relatively low energy and momentum resolutions, and very recently we have carried out systematic high-resolution ARPES experiments on Na_xWO_3 for the full range of x .^{20–23} Moreover, due to the previous low energy and angular resolution of the experimental data, it was difficult to compare the experimental results with available band calculations.^{24–26} The evolution of electronic structure with x in the metallic regime was also not clear from the previous studies. Hence a high-resolution ARPES is absolutely necessary to experimentally establish the band structure, evolution of electronic structure with Na doping, and to elucidate the mechanism behind the MIT in Na_xWO_3 .

2. Crystal Growth and Experimental Setup

2.1. Single crystal growth and characterization

We have investigated the electronic properties of Na_xWO_3 single crystals with compositions $x = 0.025, 0.3, 0.58, 0.65, 0.7$ and 0.8 . The insulating Na_xWO_3 single crystals ($x = 0.025$) were grown from high temperature solution of 15 mol% of Na_2O with WO_3 by a slow cooling method.²⁷ The crystals were found to have orthorhombic structure with lattice parameters $a = 7.311 \pm 0.003$ Å, $b = 7.523 \pm 0.003$ Å, and $c = 3.85 \pm 0.001$ Å. The most successful method to make large metallic single crystals is by an electrolytic reaction between molten mixtures of tungstate and tungsten oxide. Metallic single crystals of Na_xWO_3 ($x = 0.3, 0.58, 0.65, 0.7$ and 0.8) were grown by the fused salt electrolysis of Na_2WO_4 and WO_3 , as described by Shanks.²⁸ The Laue, Scanning Electron Microscope (SEM), and resistivity measurements show that the crystals are single crystal and metallic. The x values were obtained from the measured lattice parameters $a = 3.7845 + 0.082x$ Å, as described by Brown and Banks.¹⁰

Fig. 4. A typical modern high-resolution angle-resolved photoemission spectrometer at Tohoku University, Sendai, Japan.

2.2. High-resolution ARPES

High-resolution ARPES measurements were performed in the photoemission laboratory, Tohoku University, Japan (see Fig. 4) using a VG-SCIENTA SES2002 analyzer with a high-flux discharge lamp and a toroidal grating monochromator. The He I α ($h\nu = 21.218$ eV) resonance line was used to excite photoelectrons. ARPES measures the kinetic energy and angle of emitted photoelectrons with respect to the surface normal, when light shines on the surface of a solid. The conservation laws of energy and in-plane momentum in photoemission process allows us to determine the energy and momentum of electrons in solids, or in other words, their electronic band dispersion. The Fermi surface (FS) measurements at different photon energies (except for the He I α photons) were measured with a linear horizontal (p type) polarization of the Apple II nonperiodical undulator available at the low-energy branch of the APE-INFN beamline installed at the Elettra synchrotron, Italy. The energy and angular (momentum) resolutions were set at 5–25 meV and 0.2° , respectively. The measurements were performed at 14–300 K in a vacuum better than 5×10^{-11} Torr base pressure. A clean surface for photoemission measurements was obtained by *in situ* cleaving along (001) surface. We measured ARPES spectra within 24 hours after cleaving, during which we did not observe any significant changes in the spectra indicative of the contamination/degradation of the sample

surface. The Fermi level (E_F) of the sample was compared to that of a gold film evaporated on the sample substrate.

3. Theoretical Band Calculations

We have performed *ab initio* band structure calculations for WO_3 and NaWO_3 using projected augmented wave potential^{29,30} as implemented in the Vienna *ab initio* simulation package (VASP) code.³¹ A k -points mesh of $8 \times 8 \times 8$ with lattice constant of 3.78 Å and 3.86 Å for WO_3 and NaWO_3 , respectively, and the generalized gradient approximation (GGA) for the exchange were used for the calculation. We have simulated electron doping in our calculations by a rigid band shift of the band structure and the corresponding calculated FS was compared with the experiment. We have used the scissor operator technique to independently align the calculated valence and conduction-band structure with the experiment due to the underestimation of the band gap in GGA exchange based calculations.

4. Results and Discussions

We have measured high-resolution ARPES spectra on both insulating ($x = 0.025$) and metallic ($x = 0.3, 0.58, 0.65, 0.7$ and 0.8) Na_xWO_3 and the results are discussed in the following subsections.

4.1. Valence-band region

4.1.1. Insulating regime

The valence-band ARPES spectra of insulating Na_xWO_3 for $x = 0.025$, which has x well below the critical composition, is measured with He I α photons at 130 K. Figures 5(a) and 5(b) show ARPES spectra^{21,22} along $\Gamma(X)$ – $X(M)$ and $\Gamma(X)$ – $M(R)$ directions in the Brillouin zone (BZ) of Na_xWO_3 as shown in Fig. 5(c), respectively. As we have mentioned above [see Fig. 3(a)], in sodium tungsten bronzes, the Fermi level is situated in the conduction band for all the compositions. The bottom of the conduction band in Na_xWO_3 for $x = 0.025$ lies at 0.5 eV binding energy as clearly visible around $M(R)$ point, whereas the top of the valence band extends up to 2.5 eV indicating a large (~ 2 eV) energy gap. In fact, this large energy gap corresponds to the hard band gap observed in insulating WO_3 . There are mostly three prominent peaks observed in the valence band, one is at 4.0 eV (in both the high symmetric directions) along with two other broad peaks at 6.0 and 7.4 eV around the $\Gamma(X)$ point, which disperse downward while moving towards zone boundaries. In Fig. 5(d), we show the experimental valence-band structure^{21,22} of Na_xWO_3 for $x = 0.025$ and it was obtained by taking the second derivative of the ARPES spectra shown in Figs. 5(a) and 5(b). The pseudopotential band structure for cubic WO_3 is also presented for comparison. We shift the calculated E_F of WO_3 upward to overlap with experimental bands. We find dispersive band at the $\Gamma(X)$

Fig. 5. Valence-band ARPES spectra of Na_xWO_3 for $x = 0.025$ measured at 130 K along (a) $\Gamma(X)-X(M)$ and (b) $\Gamma(X)-M(R)$ directions. (c) Cubic Brillouin zone showing high symmetric lines of NaWO_3 . (d) Experimental valence-band structure obtained from ARPES experiments. Bright areas correspond to the experimental bands. The theoretical band calculation of WO_3 after shifting E_F is also shown by thin solid and dashed lines for comparison.

point along with bands at $X(M)$ and $M(R)$ points which are not predicted in the band calculation. The top of the valence band at 2.5 eV around the $\Gamma(X)$ point is also not predicted in the band calculation. Nevertheless the band around 4.0 eV at $\Gamma(X)$, which highly disperses along both $\Gamma(X)-X(M)$ and $\Gamma(X)-M(R)$ directions, is in good agreement with the band calculation. It is found from the band calculation that the valence band of Na_xWO_3 for $x = 0.025$ consists of mostly the O $2p$ states along with a small admixture of bonding W $5d$ states.

To investigate the temperature dependence of the valence-band spectra, we carried out photoemission spectroscopy (PES) of Na_xWO_3 for $x = 0.025$ around the $\Gamma(X)$ point (within acceptance angle of detector) with variation of temperature,^{21,22}

Fig. 6. Valence-band PES spectra of Na_xWO_3 for $x = 0.025$ at several temperatures showing the signature of polaron formation at valence-band edge, 2.5 eV. The inset shows the temperature dependence of the intensity ratio of the 2.5 eV peak to the 4.0 eV peak.

and the results are shown in Fig. 6. Our PES spectra see mostly the angle-integrated spectra around the $\Gamma(X)$ point and all the spectra are normalized under the curve within the energy range shown in the figure. We clearly observe the variation of the intensity of the 2.5 eV peak with temperature. The existence of 2.5 eV peak at the $\Gamma(X)$ point is not predicted from the band calculation. To clarify whether this feature corresponds to the surface states or not, we measured PES spectra with He $\text{II}\alpha$ ($h\nu = 40.814$ eV) photons, which is much more surface sensitive than the He $\text{I}\alpha$ resonance line. We do not see any reasonable density of states (DOS) at 2.5 eV due to the three-dimensional band structure of this band implying its bulk origin.

It is believed that at low sodium doping levels, the sodium tungsten bronzes are nonmetallic with localized W^{5+} and W^{6+} ions and show polaronic states.^{32,33} Polarons can be formed in the insulating system, particularly when the conduction electrons are in a comparatively narrow d band and are contributed by donors distributed at random in the lattice. The polaron formation in the lightly-doped tungsten bronzes was studied with electron spin resonance, optical absorption, and Raman spectroscopy.^{32,34} The conduction electrons are self-trapped by inducing an asymmetric local deformation of the lattice. Even if the electron is confined to a single lattice site, this type of trapping does not imply localization. The tunneling between different lattice sites is still relevant and a self-trapped carrier resides in an itinerant polaron state.³⁵ This is most likely to occur when the band edge is degenerate and the valence-band edge is more often degenerate than the conduction-band edge, so that holes are more likely to be self-trapped than electrons. In the inset of Fig. 6, we show the intensity ratio of valence-band edge (2.5 eV peak) to 4 eV peak. We find that the intensity of 2.5 eV peak decreases with increasing temperature and reaches minimum above 225 K. We think that the reduction in the intensity of 2.5 eV peak is due to the breakdown of polaron formation at higher temperatures (above 225 K). Above this temperature, the holes/electrons are no longer self-trapped. To study how this 2.5 eV peak behaves with respect to wave vector k , in different temperatures, we measured the ARPES spectra at 230 K in both high symmetric directions, and the results are shown in Figs. 7(a) and 7(b). We clearly observe the reduction in intensity of 2.5 eV peak around the $\Gamma(X)$ point as compared to Figs. 5(a) and 5(b) ($T = 130$ K). We have plotted the intensity variation of the 2.5 eV peak with respect to k along $\Gamma(X)$ – $X(M)$ direction for 130 K and 230 K, and the result is shown in Fig. 7(c).²² The intensity around $\Gamma(X)$ point decreases as we move from 130 K to 230 K, whereas the intensity increases in other k -points away from $\Gamma(X)$ point ($k = 0$). A polaron can be considered as a local deformation/defect in the lattice and a truly localized defect level is derived primarily from the $\Gamma(X)$ point ($k = 0$) with far less weight from other k -points. A more delocalized defect level is derived from k -points other than Γ .³⁶ To our best knowledge, the temperature dependence of the polaronic features is the first observation of the dynamics of the polaron. As the polaron becomes more delocalized, there is spectral weight transfer from Γ point to other k -points. In Fig. 6 we mainly observe the intensity around Γ point, and as a result, the intensity decreases with increasing temperature. The optical absorption of W^{5+} in WO_3 shows signature of polaron formation at low temperature and vanishes at 300 K,³² providing an additional support to our conclusion that the increase in the intensity of valence-band edge below 225 K is likely due to the formation of polaron. The polaron can split/broaden the edge of the valence band, but due to the temperature-induced broadening in the spectra, we did not find any significant splitting/broadening of the band edge with temperature. We observed that this 2.5 eV feature also survives into the metallic regime. The weakly dispersive nature of the states suggests that the presence of intrinsic defects could be a possible origin. Earlier theoretical

Fig. 7. Valence-band ARPES spectra of Na_xWO_3 for $x = 0.025$ measured at 230 K along (a) $\Gamma(X)$ - $X(M)$ and (b) $\Gamma(X)$ - $M(R)$ directions. (c) Intensity variation of 2.5 eV peak with respect to wave vector, k along $\Gamma(X)$ - $X(M)$ direction at 130 K and 230 K.

work³⁷ on amorphous WO_3 suggests that oxygen vacancy creates in-gap states and these states by nature of their origin are weakly dispersive. The filling of conduction band in WO_3 can be achieved by two means, either by a deficiency of oxygen or by addition of sodium metal or both. It was observed that the doping by means of only sodium-metal addition and oxygen vacancy are fundamentally different. Addition of Na does not affect the microscopic structure much and results in a filling of conduction band states only, while removal of oxygen triggers significant relaxations in the system as the W atoms interact with the “others” more easily and such interaction significantly decreases the W-W distance in the system. As a result, new deep in-gap states that are clearly separated from the conduction bands develop. Hence, we interpret that the 2.5 eV feature arises from the polaronic state formed by oxygen vacancies which exhibits strong temperature dependence at low concentrations.

Fig. 8. Valence-band ARPES spectra of Na_xWO_3 for $x = 0.3, 0.58$ and 0.65 measured at 14 K with He I α photons (21.218 eV) along (a) $\Gamma(X)$ – $X(M)$ direction for $x = 0.3$, (b) and (c), $\Gamma(X)$ – $M(R)$ direction for $x = 0.58$ and 0.65 respectively.

4.1.2. Metallic regime

Figure 8 shows the valence-band ARPES spectra²⁰ of metallic Na_xWO_3 for $x = 0.3, 0.58$ and 0.65 measured at 14 K with He I α photons along the $\Gamma(X)$ – $X(M)$ (for $x = 0.3$) and $\Gamma(X)$ – $M(R)$ (for $x = 0.58$ and 0.65) high symmetry lines in the BZ. We can see a large (~ 2 eV) energy gap between the bottom of the conduction band and the top of the valence band similar to Na_xWO_3 for $x = 0.025$ (see Fig. 5). A clear Fermi edge is visible in these metallic compounds. There are three prominent peaks visible around the $\Gamma(X)$ point. In Na_xWO_3 for $x = 0.3$, peaks are not very sharp due to the presence of disorder. A non-dispersive peak at the top of the valence band at the $\Gamma(X)$ point gradually loses its intensity while moving towards zone boundaries, and once again becomes prominent at zone boundaries. For $x = 0.58$ and 0.65 , the most prominent peak in the valence band is seen around 4.1–4.3 eV at the $\Gamma(X)$ point and disperses downward around the $\Gamma(X)$ point.

Figure 9 shows the valence-band ARPES spectra²⁰ of Na_xWO_3 for $x = 0.7$ and 0.8 , measured at 14 K along both the $\Gamma(X)$ – $X(M)$ and $\Gamma(X)$ – $M(R)$ high-symmetry lines. We find that all the spectral features are essentially similar in both compounds. However, in the $\Gamma(X)$ – $X(M)$ direction, the intense peak at 4.3 eV does not disperse as compared to the $\Gamma(X)$ – $M(R)$ direction [see Figs. 9(b) and 9(d)]. We clearly see four peaks near $\Gamma(X)$ point [Fig. 9(d)]. Two peaks between 4 to 6 eV merge to a single intense peak at 4.3 eV around $\Gamma(X)$. With increasing Na concentration in highly metallic Na_xWO_3 , all the peaks become more intense and sharper. This is attributed to the decrease of disorder in the system. No additional bands are found to emerge in the relevant energy window with Na doping, which suggest that a rigid band model is adequate.

Fig. 9. Valence-band ARPES spectra of Na_xWO_3 measured at 14 K for $x = 0.7$ along (a) $\Gamma(X)$ – $X(M)$ and (b) $\Gamma(X)$ – $M(R)$ directions and for $x = 0.8$ along (c) $\Gamma(X)$ – $X(M)$ and (d) $\Gamma(X)$ – $M(R)$ directions.

In Fig. 10, we show the valence band-edge region at the $\Gamma(X)$ point of the highly metallic compositions (above $x = 0.5$) studied here.^{20,22} To confirm whether the rigid band model is appropriate or not in the highly metallic Na_xWO_3 , we have excluded the $x = 0.3$ metallic composition since it is very close to MIT. A clear shift in the valence-band edge is observed as the Na content is increased. We have shifted the spectra (after normalizing the area under the curve), superimposed them and determined the shift to be ~ 0.24 eV as x is varied from 0.58 to 0.8. The inset shows the theoretically computed energy shift calculated from a rigid band model. The experimental shift (0.24 eV) is quite close to the theoretically computed shift, ~ 0.3 eV. Within a rigid band model [see Fig. 3(a)], the band structure of

Fig. 10. Comparison of ARPES spectra near valence-band edge in highly metallic Na_xWO_3 for $x = 0.58, 0.65, 0.7$ and 0.8 . The inset shows the calculated Fermi energy shift with Na doping x from the rigid band model.

both WO_3 and NaWO_3 should be identical, with E_F at different positions. As Na content increases in WO_3 , the conduction band fills up and E_F gradually moves upward. Hence we conclude that rigid band model is quite appropriate for highly metallic Na_xWO_3 , where the doped electrons from Na merely fill up the conduction band.

We have mapped out the band structure of Na_xWO_3 for $x = 0.3, 0.58$ and 0.65 along the $\Gamma(X)-X(M)$ (for $x = 0.3$) and $\Gamma(X)-M(R)$ (for $x = 0.58, 0.65$) directions and the results are shown in Fig. 11 (Ref. 20). The experimental band structure has been obtained similar to Na_xWO_3 for $x = 0.025$ [see Fig. 5(d)]. We also show the pseudopotential band structure of cubic Na_xWO_3 as thin solid and broken lines for comparison. We see primarily four bands in the valence band region. The experimental band structures are essentially similar for both $x = 0.58$ and 0.65 along the $\Gamma(X)-M(R)$ direction. The top of the valence band [Figs. 11(b) and 11(c)] at 3.3 eV binding energy around $\Gamma(X)$ point is not predicted in the band calculation. This flat feature may be dominated by the angle-integrated type background reflecting the strong intensity of the band at the $M(R)$ point. The intensity along the $\Gamma(X)-M(R)$ direction at 4.3 eV arises due to angle-integrated type background from the strong intensity of bands at $\Gamma(X)$, and vanishes with

Fig. 11. Experimental valence-band structure of Na_xWO_3 for $x = 0.3, 0.58$ and 0.65 obtained from ARPES experiments along (a) $\Gamma(X)$ – $X(M)$ direction for $x = 0.3$, (b) and (c) $\Gamma(X)$ – $M(R)$ direction for $x = 0.58$ and 0.65 , respectively. Bright areas correspond to the experimental bands. The theoretical band calculation of NaWO_3 is also shown by thin solid and dashed lines for comparison.

the decrease of disorder in Na_xWO_3 . The gross features of experimental valence band at higher binding energy ($4 \sim 8$ eV) can be explained by the *ab initio* band structure calculations. As explained before, the valence band ($3 \sim 9$ eV) consists of mostly O $2p$ character of Na_xWO_3 with a small admixture of bonding W $5d$ character.

Figure 12 shows the experimental band mapping of Na_xWO_3 for $x = 0.7$ and 0.8 along the $\Gamma(X)$ – $X(M)$ and $\Gamma(X)$ – $M(R)$ high symmetry lines, together with the *ab initio* band structure.²⁰ Both band structures for $x = 0.7$ and 0.8 along $\Gamma(X)$ – $X(M)$ and $\Gamma(X)$ – $M(R)$ directions are essentially similar. In both compositions we find two flat non-dispersive bands at 3.5 and 4.5 eV around the $\Gamma(X)$ point along the $\Gamma(X)$ – $X(M)$ direction similar to $x = 0.3$ composition [Fig. 11(a)]. The band structures along the $\Gamma(X)$ – $M(R)$ direction for $x = 0.7$ and 0.8 are similar to those of $x = 0.58$ and 0.65 , showing four dispersive bands in the valence band region. Comparison of valence band structures of $x = 0.58$ and 0.8 shows that all the bands in valence band regime move downward rigidly. Thus with increasing x in Na_xWO_3 , the Na $3s$ electrons just fill the W $5d$ t_{2g} conduction band and change the E_F position, consistent with the rigid band model appropriate for the highly metallic compositions (above $x = 0.5$) studied here.

4.2. Near E_F region

To investigate the conduction band in more detail, we have carried out high-resolution ARPES measurements with a smaller energy interval and a higher signal-to-noise ratio near E_F .

Fig. 12. Experimental valence-band structure of Na_xWO_3 obtained from ARPES experiments for (a) $x = 0.7$ and (b) $x = 0.8$ along high symmetric directions. The theoretical band calculation of NaWO_3 is also shown for comparison.

4.2.1. Insulating regime

We have measured ARPES spectra in the near E_F region of Na_xWO_3 for $x = 0.025$ at 130 K along both the high symmetric directions and the results are shown in Figs. 13(a) and 13(b) (Refs. 21 and 22). We observe a peak near 0.45 eV at $\Gamma(X)$, which disperses upward around the $\Gamma(X)$ point. Similar feature is also observed at both the $X(M)$ and $M(R)$ points. This dispersive peak represents the conduction band of Na_xWO_3 for $x = 0.025$, which never crosses E_F , showing that the system is insulating. Figure 13(c) shows the plot of ARPES intensity near E_F .^{21,22} We find an electron-like pocket at the $\Gamma(X)$ point, whose dispersion agrees satisfactorily with the band calculation. The conduction band is assigned as the W 5d t_{2g} orbital from the band calculation. Similar electron-like pocket is also observed at the $X(M)$ and

Fig. 13. ARPES spectra near E_F of Na_xWO_3 for $x = 0.025$ measured at 130 K along (a) $\Gamma(X)$ - $X(M)$ and (b) $\Gamma(X)$ - $M(R)$ directions. Vertical bars are a guide to eyes for band dispersion. (c) Experimental near E_F band structure along the high symmetric directions. Theoretical band structure of WO_3 after shifting E_F is also shown by thin solid and dashes lines for comparison.

$M(R)$ points, contrary to the band calculation. This may be due to the surface reconstruction, which we discuss later. The insulating behavior arises from the Anderson localization of all the states near E_F due to the strong disorder caused by inserting Na in a WO_3 lattice. As a result of the localization, a soft Coulomb gap arises at E_F and consequently the DOS vanishes at E_F . This gap arises due to the long-range interaction of the electrons trapped due to the strong disorder caused by the Na doping. Hence, we conclude that due to the Anderson localization, all the states near E_F are localized and a soft Coulomb gap opens at E_F . This would be responsible for its insulating properties. The possibility of splitting of the band due to electron correlation at the chemical potential (E_F) into two bands, originally proposed by Mott,³⁸ is unlikely in the case of Na_xWO_3 . Such correlation-driven gaps at E_F can be formed only if the band has integral occupancy. This is obviously not the case for any arbitrary value of x in general; specifically, the occupancy of W $5d$

is only a fractional 0.025 per site in Na_xWO_3 for $x = 0.025$. Moreover, the Coulomb repulsion (U) is expected to be weak and the tungsten $5d$ bandwidth (W) large in Na_xWO_3 to satisfy the Mott–Hubbard criterion of $U/W \gg 1$. On the other hand, the low DOS at band bottom for the small x value favors localization of states due to disorder effects. The weak localization,³⁹ which arises from the multiple elastic scattering of carriers, leading to quantum interference, can also make the system insulating but is not feasible in the low-doped sodium tungsten bronzes. We explain this as follows: (i) if some collisions of the conduction electrons are inelastic, then the quantum interference cannot take place. These inelastic collisions can either be with other conduction electrons or with phonons above the Debye temperature. Hence, with variation of temperature one should see an insulator-to-metal like change, which does not occur in sodium tungsten bronzes. (ii) This effect is significant when the mean free path, l , is small, and thus typically seen in non-crystalline materials. There are few papers on the development of surface superconductivity in low-doped sodium tungsten bronzes. Reich and Tsabba⁴⁰ reported surface superconductivity with T_c as high as 91 K in the lightly-doped sodium tungsten bronzes, $\text{Na}_{0.05}\text{WO}_3$. Our data near E_F does not support this idea. We did not observe any finite DOS at E_F above T_c with our high-resolution measurements (Fig. 13). Hence we conclude that there is no such superconductivity on the surface of the lightly-doped sodium tungsten bronzes.

4.2.2. *Metallic regime*

Figure 14 shows the high-resolution ARPES spectra near E_F of Na_xWO_3 for $x = 0.58, 0.65, 0.7$ and 0.8 measured at 14 K with He I α photons along the $\Gamma(X)$ – $M(R)$ direction.²⁰ We observe a very weak broad feature near $0.9 \sim 1.0$ eV at $\Gamma(X)$, which disperses upward to form an electron-like pocket at $\Gamma(X)$ for all compositions of x . There is no signature of such a feature at $X(M)$ or $M(R)$ as observed in its insulating counterpart at He I α photon energy. We have shown only the $\Gamma(X)$ – $M(R)$ direction in figures as we are concerned about the $\Gamma(X)$ region only due to the presence of band dispersion near E_F at $\Gamma(X)$. As the Na concentration increases, this feature becomes very prominent as shown in Fig. 14(d). This behavior may be due to the decrease of disorder with increasing x in the system. From the figures, we find that the bottom of conduction band lies roughly around $0.9 \sim 1.0$ eV below E_F . The exact position of the band bottom is difficult to determine due to the very low spectral intensity at its bottom. Nevertheless, it is clear that the conduction band bottom moves downward with Na concentration similar to the trend seen for the valence band (Fig. 10). This can be explained by considering the simple rigid band shift. Since the determination of the exact position of band bottom has much more ambiguity, it is difficult to determine quantitatively the shift of the band bottom from $x = 0.58$ to 0.8 . Previous literature^{19,41–43} reported that the bandwidth of occupied conduction states appear to be almost independent of Na concentration which is not supported by our results. Since the DOS at band bottom is very low

Fig. 14. ARPES spectra near E_F of Na_xWO_3 for (a) $x = 0.58$, (b) $x = 0.65$, (c) $x = 0.7$ and (d) $x = 0.8$ measured at 14 K along the $\Gamma(X)$ – $M(R)$ direction. Vertical bars are a guide to eyes for band dispersion.

and the background is high, it was very difficult to get the exact bandwidth of the occupied states from the previous angle-integrated measurements.^{19,41–43}

Figure 15 shows the plot of ARPES intensity as a function of the wave vector and the binding energy, showing the experimental band structure near E_F for highly metallic sodium tungsten bronzes.^{20,22} We find an electron-like pocket at the $\Gamma(X)$, whose linear dispersion at E_F agrees satisfactorily with the band calculation. We find a clear variation in the spectral intensity at E_F , which suggests that the band crosses E_F at the highest intensity (k_F) region. No signature of impurity band (level) near E_F is seen in Figs. 15(a)–15(d), which rules out the development of a Na-induced impurity band (level). Hence, we conclude that the previous speculation

Fig. 15. Experimental near E_F band structure of Na_xWO_3 for (a) $x = 0.58$, (b) $x = 0.65$, (c) $x = 0.7$ and (d) $x = 0.8$ measured at 14 K along the $\Gamma(X)-M(R)$ direction of BZ. Theoretical band structure of NaWO_3 is also shown by thin, solid and dashed lines for comparison. Open circles show the highest intensity in experimental band mapping. (e) Near E_F momentum distribution curve (MDC) of Na_xWO_3 for $x = 0.8$. The gray solid line represents the MDC peak dispersion. The Fermi velocity v_F is determined from the slope, $(\delta E/\delta k)$ at E_F . (f) The effective mass (m^*/m_e) with respect to Na concentration in Na_xWO_3 .

regarding the MIT being due to the development of Na-induced impurity band (level) is not supported by our results.

In the rigid band-model with a spherical Fermi surface and rigid parabolic density of states (DOS), the density of states $N(E)$ is proportional to $E^{\frac{1}{2}}$. It is assumed that all sodium atoms are ionized in Na_xWO_3 , hence $N(E_F)$, the density of states at E_F , is proportional to $x^{\frac{1}{2}}$. However, the physical properties including the magnetic

susceptibility and the specific heat coefficient⁴⁴ γ were found to vary linearly with x . We extrapolated the band dispersion from the highest intensity points of the band mapping [shown as open circles in Figs. 15(a)–15(d)] and find that the conduction bandwidth expands with increasing x ; the experimental band dispersion is not free electron-like parabolic as proposed before. The *ab initio* band structure results also show linear band dispersion as observed experimentally. The expansion of the conduction band can be well explained by the linear increase in the DOS of the conduction band with increasing x in Na_xWO_3 . This explanation fits well with the x -dependent behavior of the specific heat and the magnetic susceptibility, which vary linearly with x for highly metallic Na_xWO_3 . The heat capacity data⁴⁴ show that the effective mass (m^*) of the conduction electrons increases monotonically with x . We determined the effective mass from the Fermi velocity v_F as shown in Fig. 15(e) for $x = 0.8$ and found a similar monotonic increase in the effective mass [Fig. 15(f)] of the conduction electrons for all x . The band mass is less than the free electron mass m_0 and agrees quantitatively with the mass found from other experiments.⁴⁵

4.3. Fermi surface topology

To determine the location of Fermi surface, generally two methods are used in ARPES. In the first method, one just follows the dispersion of bands from energy distribution curves (EDCs) and obtains the k -space point where the band actually crosses E_F . In the second method, the intensity at E_F is recorded with a series of azimuthal scans (ϕ), each step being repeated at different polar angles (θ) within a given photon energy.

4.3.1. Insulating regime

In Fig. 16(a), we show the ARPES-intensity plot at E_F as a function of two-dimensional (2D) wave vector.²¹ The intensity is obtained by integrating the spectral weight within 80 meV with respect to E_F and symmetrized, assuming the cubic symmetry. The conduction band arising from the W $5d$ t_{2g} orbital disperses upward (Fig. 13) but never crosses E_F . Our finding reveals a remnant Fermi surface even though Na_xWO_3 for $x = 0.025$ shows insulating behavior due to Anderson localization. Similar remnant Fermi surface is also observed in the other insulator, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$.⁴⁶ From the high-quality data near E_F we establish that the remnant Fermi surface observed at the $\Gamma(X)$ point in the insulating phase has a shape similar to the real Fermi surface in metallic sodium tungsten bronzes which one expects in the absence of any disorder in metallic phase and matches well to the band calculation. We find similar Fermi surfaces at $X(M)$ or $M(R)$ and we infer that this is due to the surface reconstruction. We carried out the low-energy electron diffraction (LEED) for the (001) cleaved surface with primary energy of 54 eV at 130 K and the result is shown in Fig. 16(b) (Ref. 21). In the LEED pattern, we see the 1×1

Fig. 16. (a) Remnant Fermi surfaces of Na_xWO_3 for $x = 0.025$ at 130 K in the first BZ. Solid and dashed circles show the highest intensity points. (b) LEED pattern of (001) cleaved surface of Na_xWO_3 for $x = 0.025$ measured with primary energy of 54 eV at 130 K. It shows the 1×1 bulk and the 2×2 surface superlattice spots.

bulk and the 2×2 surface superlattice spots. The 2×2 superlattice spots regenerate the $X(M)$ or $M(R)$ points as a new $\Gamma(X)$ point in ARPES. Hence, the surface reconstruction is confirmed from our LEED measurement. Now, we discuss in more detail the surface reconstruction, which may create 2D electronic states on the first few layers different from the bulk states. Such surface-reconstruction-derived bands were found in the ARPES spectra of Sr_2RuO_4 .⁴⁷ The rotation and deformation of the WO_6 octahedra in Na_xWO_3 for $x = 0.025$ gives rise to the orthorhombic crystal structure. In the bulk, the rotation is small and we think that the rotation of the WO_6 octahedra increases at surface due to the reduced atomic coordination, which is responsible for the surface reconstruction in Na_xWO_3 for $x = 0.025$ as similarly observed in Sr_2RuO_4 .

4.3.2. *Metallic regime*

The ARPES-intensity plots at E_F for Na_xWO_3 ($x = 0.58, 0.7$ and 0.8) as a function of the 2D wave vector are shown in Fig. 17 (Refs. 20 and 22). The intensity is obtained by integrating the spectral weight within 20 meV with respect to E_F . We calculated the Fermi surface(s) (on ΓXMX and XMRM plane) for fractional Na concentration in Na_xWO_3 ($x = 0.58, 0.7$ and 0.8) assuming rigid band shifts, which are shown by dotted lines. We observe one spherical electron-like Fermi surface centered at the $\Gamma(X)$ point, which is covered with another square-like Fermi surface. Along the $\Gamma(X)$ – $X(M)$ direction, we find only one k_F point, while along the $\Gamma(X)$ – $M(R)$ direction, there are two distinct k_F points. These two Fermi surfaces are attributed to the W $5d\ t_{2g}$ bands. On increasing the Na concentration, the Na $3s$ electrons are transferred to the W $5d\ t_{2g}$ band at E_F . Hence, the volume of the FS gradually increases in accordance with the increase of the Na concentration. The square-like FS centered at the M point is not clearly visible in Na_xWO_3 for $x = 0.58$

Fig. 17. Fermi surfaces of Na_xWO_3 for (a) $x = 0.58$, (b) $x = 0.7$ and (c) $x = 0.8$ showing electron-like pocket at the $\Gamma(X)$ point. Dotted lines around $\Gamma(X)$ point are the calculated Fermi surface(s) (on ΓXMX and XM RM plane) for fractional Na concentration based on the rigid band model.

and $x = 0.7$ but is prominent in $x = 0.8$. This FS arises from one single band, whereas the FS(s) observed at $\Gamma(X)$ point are from three bands (two from ΓXMX and one from the XM RM planes) and hence the intensity is much more enhanced around the $\Gamma(X)$ point in the ARPES experiment. The volume of calculated FS and experimental FS matches well for all highly metallic compositions studied here. A rigid shift of the Fermi energy is found to give a qualitatively good description of the Fermi surface.

In the insulating region, we found electron-like remnant FSs at $X(M)$ and $M(R)$ points in contradiction to the band calculation. The evolution of remnant FSs in the insulating phase of Na_xWO_3 at other symmetry points is explained by the surface reconstruction. However, it is still doubtful whether or not such a kind of surface reconstruction exists in the highly metallic Na_xWO_3 surfaces. To understand this issue, we have mapped out FS measurements at different bulk and surface-sensitive photon energies on metallic Na_xWO_3 . From the universal curve [Fig. 18(a)] (Ref. 23), we infer that the electron escape depth slowly decreases from the He I α (21.2 eV) to 42 eV photon energy. Hence we mainly map from more bulk-sensitive FS to highly surface-sensitive FS with increasing photon energy from 21.2 to 42 eV. Figure 18(b) shows the momentum cut in k_z - k_x plane for $k_y = 0$, where the ARPES intensity in Figs. 17(c) and 19(a)–19(c) were actually measured.²³ We have used 21.2, 26, 32, and 42 eV photon energies for FS mapping, which are shown in Figs. 17(c) and 19(a)–19(c), respectively. The FSs shown in Figs. 19(a)–19(c) are obtained by integrating the spectral weight within 30 meV with respect to E_F for a series of azimuthal scans (ϕ) and this step being repeated at different polar angles (θ) for a given photon energy. We calculated the FS(s) (on ΓXMX and XM RM plane) for fractional Na concentration in Na_xWO_3 at $x = 0.8$, by assuming the rigid-band shift shown by dotted lines. We observe one spherical electron-like

Fig. 18. (a) Universal curve: Electron escape depth as a function of their kinetic energy, (b) momentum position of ARPES cuts in k -space for various photon energies.

Fig. 19. Fermi surfaces of Na_xWO_3 for (a) 26 eV, (b) 32 eV, and (c) 42 eV photons. FS shows an electron-like pocket at $\Gamma(X)$ point for the He Iα photons, while similar electron-like pockets are also observed at $X(M)$ and $M(R)$ points with higher photon energies, likely due to the surface reconstruction. Dotted lines around $\Gamma(X)$ point are the calculated FSs (on ΓXMX and XMRM plane) for fractional Na concentration based on the rigid band model.

FS centered at the $\Gamma(X)$ point, which is covered with another square-like FS. It is clearly seen that the FS at 21.2 eV photons [Fig. 17(c)] matches well with the theoretical prediction and there is no signature of the surface reconstruction, which suggests that the obtained FSs centered at $\Gamma(X)$ point are of bulk origin. As soon as we move toward higher photon energy (i.e. 26–42 eV), we clearly recognize reconstructed spherical electron-like FS at $X(M)$ and $M(R)$ points, similar to the

Fig. 20. Projection of first two layers of WO_6 octahedra in (a) bulk and (b) surface of Na_xWO_3 along (001) direction. The combined effect of rotation and deformation of WO_6 octahedra gives rise to the superstructure at the surface of Na_xWO_3 .

one at $\Gamma(X)$ point. The reconstructed FS is most clearly visible for 42 eV photons [Fig. 19(c)], which is supposed to be the most surface-sensitive photon energy in the range of photon energies in this study. It is noted that similar surface reconstruction at $X(M)$ and $M(R)$ points is also observed in insulating $\text{Na}_{0.025}\text{WO}_3$, even at 21.2 eV photons.²¹ The rotation and deformation of the WO_6 octahedra in insulating $\text{Na}_{0.025}\text{WO}_3$ give rise to the orthorhombic crystal structure and that reflects strongly on its surface, giving rise to surface reconstruction even in relatively bulk-sensitive incident photon energy of 21.2 eV. Although the average crystal structure of bulk $\text{Na}_{0.8}\text{WO}_3$ derived from X-ray diffraction is cubic, we think that the structure of first few layers from the surface may be different due to reduced atomic coordinations, which may be responsible for the observed reconstructed FS/bands at the $X(M)$ and $M(R)$ points.

In insulating phase, the surface reconstruction at the $M(R)$ point is stronger than $X(M)$ point whereas in metallic phase, it is found to be opposite. In Fig. 20, we show schematic view of the projection of two layers of WO_6 octahedra along (001) direction in bulk and surface of $\text{Na}_{0.8}\text{WO}_3$ (Ref. 23). In perovskite structure, two types of critical distortion would appear: (i) rotation of WO_6 octahedra, giving rise to tilted structures, and (ii) deformation of the individual WO_6 octahedra and/or displacement of the W atoms from their central positions. We believe that, in bulk $\text{Na}_{0.8}\text{WO}_3$, there is no or very small distortion of WO_6 octahedra since the system has less disorder due to high doping of Na atom in WO_3 lattice, as shown in Fig. 20(a). On the other hand, the first few layers of $\text{Na}_{0.8}\text{WO}_3$ from the surface may deviate from the true bulk structure, and would show combined effect of rotation and deformation of WO_6 octahedra that gives rise to the $p(2 \times 2)$ superstructure at the surface [see Fig. 20(b)]. As a comparison with insulating $\text{Na}_{0.025}\text{WO}_3$, we

believe that the insulating phase has both $p(2 \times 2)$ and $c(2 \times 2)$ superstructures, which causes the stronger intensity of FS at $M(R)$ point as compared to that at $X(M)$ point, although the effect of matrix-element difference between the spectra at both $X(M)$ and $M(R)$ points cannot be ignored to explain these differences.

5. Conclusion

We have carried out high-resolution angle-resolved photoemission spectroscopy on Na_xWO_3 for $x = 0.025, 0.3, 0.58, 0.65, 0.7$ and 0.8 . The experimentally determined valence-band structure has been compared with the results of *ab initio* band structure calculation. It is found that in insulating Na_xWO_3 , the near E_F states are localized (Anderson localization) due to the strong disorder caused by the random distribution of Na^+ ions in WO_3 lattice. While the presence of an impurity band (level) induced by Na doping is often invoked to explain the insulating state found at low concentrations, there is no signature of impurity band (level) found in the metallic regime. Due to this disorder and Anderson localization effect, there is a long-range Coulomb interaction of conduction electrons; as a result, a soft Coulomb gap arises and the density of states vanishes exactly at E_F . We found a direct evidence of the polaron formation from the temperature dependence of the photoemission spectra. In the metallic regime, we found that the rigid shift of band structure can well explain the metallic Na_xWO_3 band structure with respect to Na doping. The linear dispersion of the conduction band at E_F explains the linear variation of thermodynamic properties including the specific heat and magnetic susceptibility. We observed electron-like Fermi surface at the $\Gamma(X)$ point as predicted from band calculation and the Fermi surface gradually increases with increasing Na concentration due to $\text{W } 5d \text{ } t_{2g}$ band filling in highly metallic systems. A rigid shift of the Fermi energy is found to give a qualitatively good description of the FS. The FS mapping with different photon energies indicates that the electronic structure of the first few layers from the surface is different from that of the bulk, possessing new FSs at the $X(M)$ and $M(R)$ points which are the replica of the FS at the $\Gamma(X)$ point. The combined effects of rotation and deformation of WO_6 octahedra giving rise to the $p(2 \times 2)$ superstructure at the surface of $\text{Na}_{0.8}\text{WO}_3$ can well explain the reconstructed FS at the $X(M)$ and $M(R)$ points found in more surface-sensitive photons.

References

1. F. Wohler, *Ann. Physik* **2** (1824) 350.
2. C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials* (Elsevier, Amsterdam, 1995).
3. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications* (VCH Verlagsgesellschaft, Weinheim, 1995).
4. J. B. Goodenough, *Progress in Solid State Chemistry*, Vol. 5, ed. H. Reiss (Pergamon, Oxford, 1971), p. 145.

5. R. Stanley, R. C. Morris and W. G. Moulton, *Solid State Commun.* **27** (1978) 1277; *Phys. Rev. B* **20** (1979) 1903.
6. M. R. Skokan, W. G. Moulton and R. C. Morris, *Phys. Rev. B* **20** (1979) 3670.
7. L. N. Caldwell, R. C. Morris and W. G. Moulton, *Phys. Rev. B* **23** (1981) 2219.
8. H. R. Shanks, P. H. Slides and G. C. Danielson, *Non-Stoichiometric Compounds, Advance in Chemistry Series*, Vol. 39 (American Chemical Society, 1963), p. 237; A. S. Ribnick, B. Post and E. Banks, *ibid.* **39** (1963) 246.
9. A. Magneli, *Nature* **169** (1952) 791.
10. B. W. Brown and E. Banks, *J. Am. Chem. Soc.* **76** (1954) 963.
11. P. W. Anderson, *Phys. Rev.* **109** (1958) 1492.
12. D. P. Tunstall and W. Ramage, *J. Phys. C: Solid State Phys.* **13** (1980) 725.
13. N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, 1990).
14. M. D. Hill and R. G. Egddell, *J. Phys. C: Solid State Phys.* **16** (1983) 6205.
15. R. L. Benbow and Z. Hurych, *Phys. Rev. B* **17** (1978) 4527.
16. M. D. Hill and R. G. Egddell, *J. Phys. C: Solid State Phys.* **16** (1983) 6205.
17. G. Hollinger, P. Pertosa, J. P. Doumerc, F. J. Himpsel and B. Reichl, *Phys. Rev. B* **32** (1985) 1987.
18. T. Wolfram and L. Sutcu, *Phys. Rev. B* **31** (1985) 7680.
19. H. Höchst, R. D. Bringans and H. R. Shanks, *Phys. Rev. B* **26** (1982) 1702.
20. S. Raj, D. Hashimoto, H. Matsui, S. Souma, T. Sato, T. Takahashi, S. Ray, A. Chakraborty, D. D. Sarma, P. Mahadevan, W. H. McCarroll and M. Greenblatt, *Phys. Rev. B* **72** (2005) 125125.
21. S. Raj, D. Hashimoto, H. Matsui, S. Souma, T. Sato, T. Takahashi, D. D. Sarma, P. Mahadevan and S. Oishi, *Phys. Rev. Lett.* **96** (2006) 147603.
22. S. Raj, H. Matsui, S. Souma, T. Sato, T. Takahashi, A. Chakraborty, D. D. Sarma, P. Mahadevan, S. Oishi, W. H. McCarroll and M. Greenblatt, *Phys. Rev. B* **75** (2007) 155116.
23. S. Raj, A. Chakraborty, D. Choudhury, T. Sato, T. Takahashi, P. Mahadevan, J. Fujii, I. Vobornik and D. D. Sarma, *Phys. Rev. B* **79** (2009) 035119.
24. L. Koop, B. N. Harmon and S. H. Liu, *Solid State Commun.* **22** (1977) 677.
25. N. E. Christensen and A. R. Mackintosh, *Phys. Rev. B* **35** (1987) 8246.
26. M. G. Stachiotti, F. Corà, C. R. A. Catlow and C. O. Rodriguez, *Phys. Rev. B* **55** (1997) 7508.
27. S. Oishi, N. Endo and K. Kiajima, *Nippon Kagaku Kaishi*, Vol. 11 (The Chemical Society of Japan, Japan, 1995), p. 891.
28. H. R. Shanks, *J. Cryst. Growth* **13–14** (1972) 433.
29. P. E. Blöchl, *Phys. Rev. B* **50** (1994) 17953.
30. G. Kresse and J. Joubert, *Phys. Rev. B* **59** (1999) 1758.
31. G. Kresse and J. Furthmüller, *Phys. Rev. B* **54** (1996) 11169; *Comput. Mat. Sci.* **6** (1996) 15.
32. O. F. Schirmer and E. Salje, *Solid State Commun.* **33** (1980) 333; *J. Phys. C* **13** (1980) L1067.
33. E. Salje and B. Guttler, *Philos. Mag. B* **50** (1984) 607.
34. R. G. Egddell and G. B. Jones, *J. Solid State Chem.* **81** (1989) 137.
35. H. DeRaedt and A. Lagendijk, *Phys. Rev. B* **27** (1983) 6097; H. Lowen, *ibid.* **37** (1988) 8661; J. Ranninger and U. Thibblin, *ibid.* **45** (1992) 7730.
36. G. F. Koster and J. C. Slater, *Phys. Rev.* **95** (1954) 1167.
37. G. A. de Wijs and R. A. de Groot, *Phys. Rev. B* **60** (1999) 16463.
38. N. F. Mott, *Phil. Mag.* **35** (1977) 111.
39. G. Bergmann, *Phys. Rev. B* **28** (1983) 2914; *Phys. Rep.* **107** (1984) 1.

40. S. Reich and Y. Tsabba, *Eur. Phys. J. B* **9** (1999) 1.
41. M. Campagna, G. K. Wertheim, H. R. Shanks, F. Zumsteg and E. Banks, *Phys. Rev. Lett.* **34** (1975) 738.
42. H. Höchst, R. D. Bringans, H. R. Shanks and P. Steiner, *Solid State Commun.* **34** (1980) 41.
43. G. K. Wertheim and J. N. Chazalviel, *Solid State Commun.* **40** (1981) 931.
44. F. C. Zumsteg, *Phys. Rev. B* **14** (1976) 1406.
45. M. Kielwein, K. Saiki, G. Roth, J. Fink, G. Paasch and R. G. Egdell, *Phys. Rev. B* **51** (1995) 10320.
46. F. Ronning, C. Kim, D. L. Feng, D. S. Marshall, A. G. Loeser, L. L. Miller, J. N. Eckstein, I. Bozovic and Z.-X. Shen, *Science* **282** (1998) 2067.
47. R. Matzdorf, Z. Fang, Ismail, J. Zhang, T. Kimura, Y. Tokura, K. Terakura and E. W. Plummer, *Science* **289** (2000) 746.