

Metal–insulator transition in sodium tungsten bronzes, Na_xWO_3 , studied by angle-resolved photoemission spectroscopy

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Abstract

We report high-resolution angle-resolved photoemission spectroscopy on sodium tungsten bronzes, Na_xWO_3 , which exhibit a metal–insulator transition as a function of x . We found that the near- E_F states are localized in Na_xWO_3 ($x \leq 0.25$) due to the strong disorder caused by the random distribution of Na^+ ions in the WO_3 lattice, which makes the system insulating. In the metallic regime we found that the rigid shift of band structure can explain the metallic Na_xWO_3 band structure with respect to Na doping.

Keywords: Metal–insulator transition; Angle-resolved photoemission spectroscopy; Anderson localization; Fermi surface; Na_xWO_3

Metal–insulator transition (MIT) observed in many transition-metal compounds is one of the highly studied subjects in condensed matter physics. In particular, electron correlations, disorder and evolution of impurity band are the main driving forces behind MIT associated with the localization and delocalization of carriers. Sodium tungsten bronze, Na_xWO_3 exhibits an MIT as a function of x . A high metallic conduction is obtained for $x \geq 0.25$, while the system undergoes a transition to an insulating phase with decreasing x [1].

Na_xWO_3 has a rich structural phase diagram. For $x \leq 0.5$, it exists in a variety of structural modifications [2], while for $x \geq 0.5$, Na_xWO_3 is a metallic with perovskite-type crystal structure. In Na_xWO_3 structure, corner-sharing WO_6 octahedra form a three-dimensional lattice

with the Na^+ ions occupying 12-O-coordinated cubo-octahedral cavities. 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 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, the band structure of both WO_3 and NaWO_3 should be identical, with E_F at different positions. In Na_xWO_3 the Na 3s electrons are transferred into the W 5d t_{2g} band and the system becomes metallic for $x \geq 0.25$. However, for low concentration of x ($x \leq 0.25$) the material is insulating and the origin of the MIT is a long-standing problem.

Single crystals of insulating ($x = 0.025$) and cubic metallic ($x = 0.58$ and 0.8) Na_xWO_3 were grown from a high-temperature solution of $\text{Na}_2\text{O}–\text{WO}_3$ and by fused salt electrolysis of Na_2WO_4 and WO_3 , respectively. Angle-resolved photoemission spectroscopy (ARPES) measurements were performed by a GAMMADATA-SCIENTA SES-200 spectrometer with a high-flux discharge lamp. The

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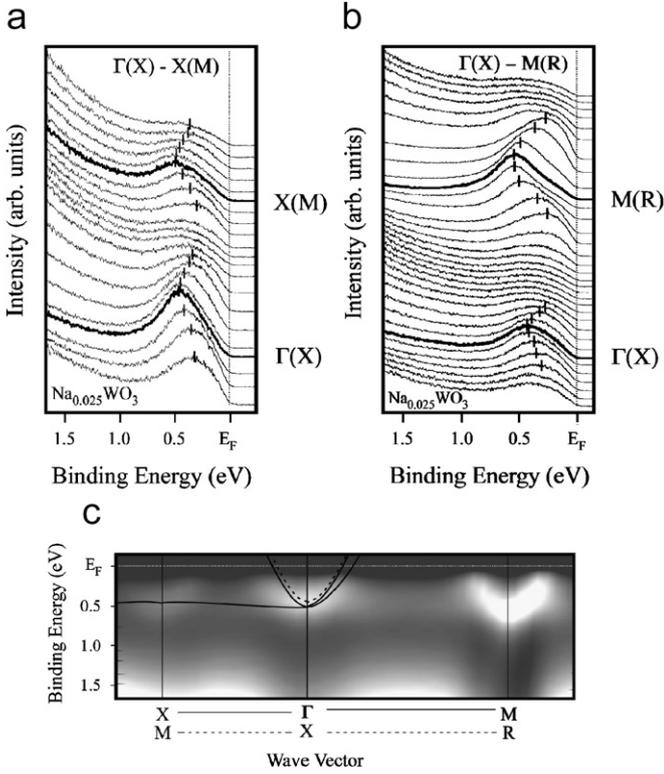


Fig. 1. ARPES spectra near E_F of insulating $\text{Na}_{0.025}\text{WO}_3$ measured along (a) $\Gamma(X)-X(M)$ and (b) $\Gamma(X)-M(R)$ in BZ at 130 K. Vertical bars are a guide to eyes for band dispersion. (c) Experimental band structure along with band calculation of WO_3 for comparison.

energy and angular (momentum) resolutions were set at 5–11 meV and 0.2° (0.01 \AA^{-1}), respectively. We have also carried out ab initio band-structure calculations for WO_3 and NaWO_3 based on the plane-wave pseudopotential method. A clean surface for photoemission measurements was obtained by in situ cleaving along $[001]$ direction.

The near- E_F ARPES spectra of insulating $\text{Na}_{0.025}\text{WO}_3$ measured at 130 K with He-I α is shown in Figs. 1(a) and (b). We observe a peak near 0.45 eV at $\Gamma(X)$, which disperses upward around $\Gamma(X)$. This dispersive peak represents the conduction band of $\text{Na}_{0.025}\text{WO}_3$, which never crosses E_F , showing that the system is insulating. Fig. 1(c) shows the plot of ARPES intensity at near- E_F region. We find an electron-like pocket at $\Gamma(X)$, 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 around both the $X(M)$ and $M(R)$ points, contrary to the band calculation. This may be due to the surface reconstruction. 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 the WO_3 lattice. Simultaneously a soft Coulomb gap arises at E_F and consequently the density of states vanishes at E_F . This gap arises due to the long-range Coulomb interaction [3] of the electrons trapped due to the strong disorder caused by Na doping. Hence, we conclude that the presence of disorder together with long-range Coulomb interactions

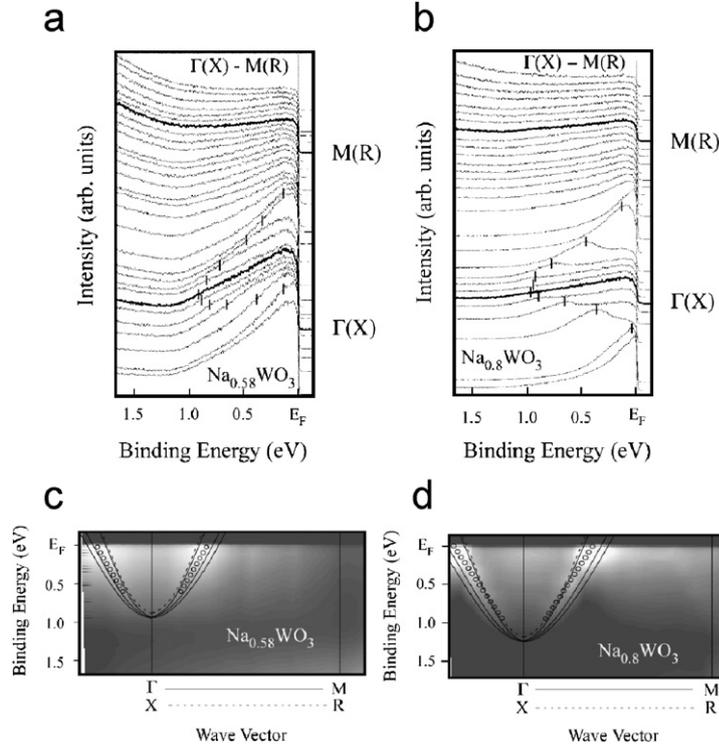


Fig. 2. ARPES spectra near E_F of metallic (a) $\text{Na}_{0.58}\text{WO}_3$, and (b) $\text{Na}_{0.8}\text{WO}_3$ measured along $\Gamma(X)-M(R)$ in BZ at 14 K. Vertical bars are a guide to eyes for band dispersion. (c) and (d) show experimental band structure of $\text{Na}_{0.58}\text{WO}_3$ and $\text{Na}_{0.8}\text{WO}_3$, respectively, along with band calculation of NaWO_3 for comparison. Open circles show the highest intensity in experimental band mapping.

leads to the formation of a soft Coulomb gap at E_F in this system, this being responsible for its insulating properties.

Figs. 2(a) and (b) show the high-resolution ARPES spectra near E_F of Na_xWO_3 for $x = 0.58$ and 0.8 measured at 14 K with He-I α photons along $\Gamma(X)-M(R)$ directions in the Brillouin zone (BZ). We observe a very weak broad feature near 1.0 eV at $\Gamma(X)$, which disperses upward to form an electron-like pocket at $\Gamma(X)$ for all metallic compositions of x . There is no signature of such a feature at $M(R)$ as observed in the insulating sample. As the Na concentration increases, this feature becomes very prominent as shown in Fig. 2(b). This behavior may be due to the decrease of disorder with increasing x in the system. Figs. 2(c) and (d) show the plot of ARPES intensity as a function of the wave vector and the binding energy, showing the experimental band structure near E_F . In both figures the bottom of the conduction band lies roughly around 0.9~1.1 eV below E_F . The exact position of the band bottom is difficult to determine due to the very low spectral

intensity at the band bottom, nevertheless, it is clear that the conduction band bottom moves downward with increasing Na concentration similar to the trend seen for the valence band. This can be well explained by considering the simple rigid band shift.

In conclusion, the insulating behavior arises in Na_xWO_3 because of the strong disorder caused by the random distribution of Na^+ ions in the WO_3 lattice. In the metallic region we conclude that the rigid shift of band structure can well explain the observed metallic Na_xWO_3 band structure with respect to increasing Na content.

References

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