

**Electronic Supplementary Information for: “*The electronic structure and the formation of polarons in Mo-doped BiVO<sub>4</sub> measured by angle-resolved photoemission spectroscopy*”**

Mansour Mohamed,<sup>1,2</sup> Matthias M. May,<sup>3</sup> Michael Kanis,<sup>3,4</sup> Mario Brützam,<sup>5</sup> Reinhard Uecker,<sup>5</sup> Roel van de Krol,<sup>3</sup> Christoph Janowitz,<sup>1</sup> and Mattia Mulazzi<sup>1,6</sup>

<sup>1</sup>*Institut für Physik, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany.*

<sup>2</sup>*Department of Physics, Faculty of Science, Assiut University, 71515 Assiut, Egypt.*

<sup>3</sup>*Institute for Solar Fuels, Helmholtz-Zentrum Berlin, D-14109 Berlin, Germany.*

<sup>4</sup>*OUT e.V., D-12555 Berlin, Germany.*

<sup>5</sup>*Leibniz-Institut für Kristallzüchtung, D-12489 Berlin, Germany.*

<sup>6</sup>*Institute Functional Oxides for Energy-Efficient IT, Helmholtz-Zentrum Berlin, D-14109 Berlin, Germany*

In ESI Fig. 1 we show the dispersion measured using the second angular degree of freedom of our manipulator. For these measurements, the angular step is about  $1^\circ$ , measured by tilting the sample in the plane perpendicular to the analyzer slit.

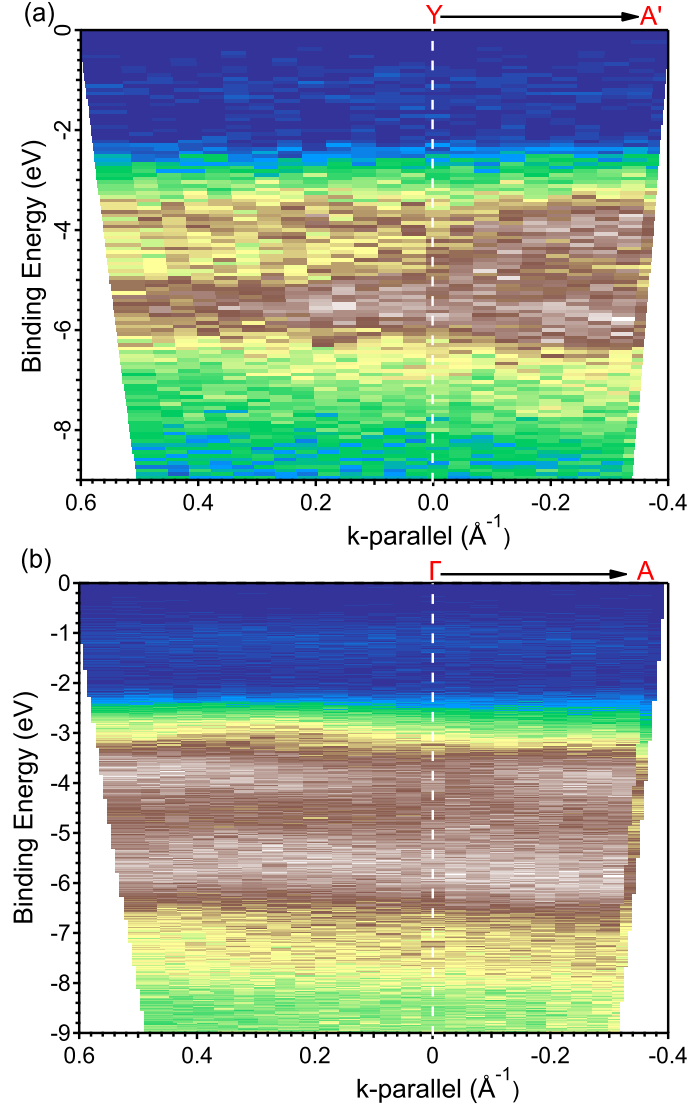


FIG. 1. ARPES maps measured perpendicular to the (a) YZ direction with a photon energy of 35 eV and (b) the  $\Gamma Z'$  direction with a photon energy of 29 eV. Since  $\text{BiVO}_4$  has a monoclinic cell, the wavevectors spanned are approximately parallel to the  $YA'$  and  $\Gamma A'$  directions, respectively (see main text).

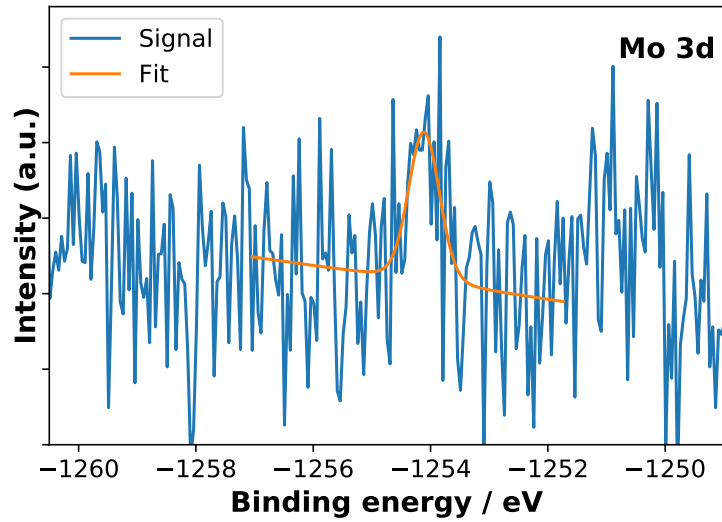


FIG. 2. X-ray photoelectron spectroscopy around the Mo 3d signal with a monochromated Al  $K_{\alpha}$  source.

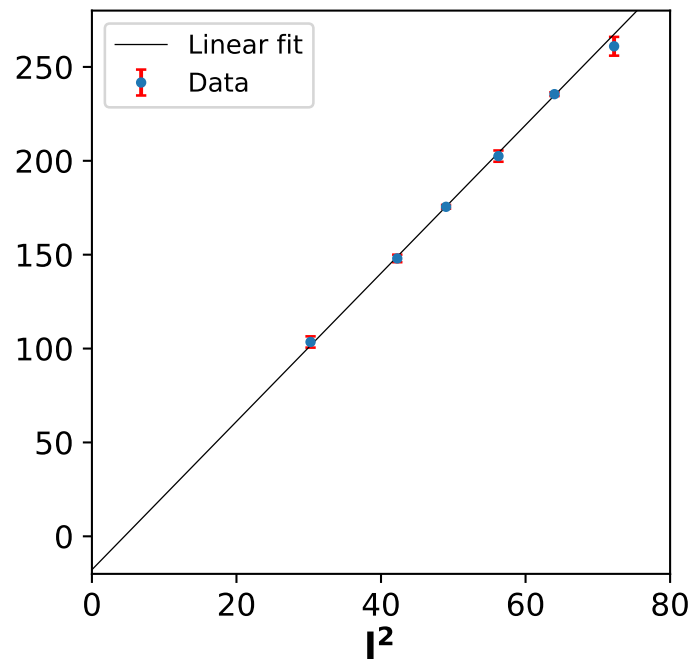


FIG. 3. Madelung graph used for the determination of the inner potential,  $U_0$ , by means of a least square fit according to  $E = l^2c - U_0$ , where  $c$  is a constant and  $E$  the energy, at which a maximum of the primary Bragg peak was observed (including half-order peaks).

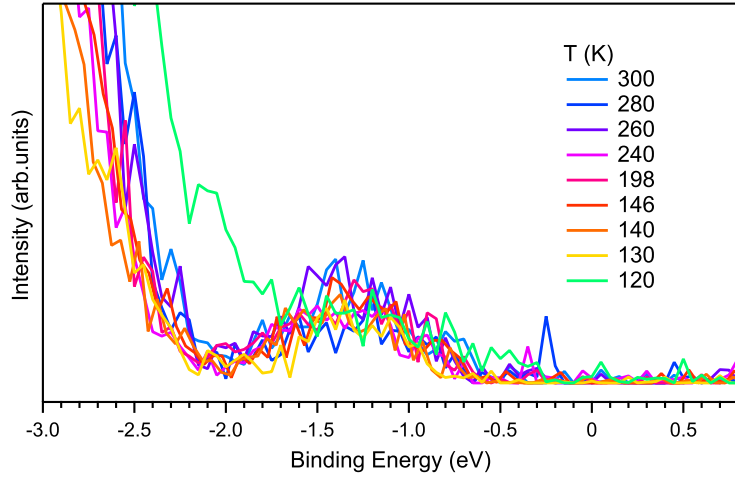


FIG. 4. Detail view of the in-gap signal from Fig. 8 (of the main manuscript) as a function of temperature. The intensity was normalised with respect to the total photon flux.