

Bulk Electronic Structure of Lanthanum Hexaboride (LaB₆) by Hard X-ray Angle-Resolved Photoelectron Spectroscopy

Supplementary material

The Supplemental Material include additional ARPES data (SM-1) ; relative angular shift of the band structure features with respect to the x-ray photoelectron diffraction pattern (SM-2); Free Electron Final State calculations (SM-3); Phonon band structure of LaB₆ (SM-4).

SM-1 Additional ARPES data

Figure SM-1a shows clearly La dispersive bands between 0 eV and 4 eV in binding energies, on the other hand, Figure SM-1b shows that, at 6 keV and room temperature, those bands are almost completely smeared out.

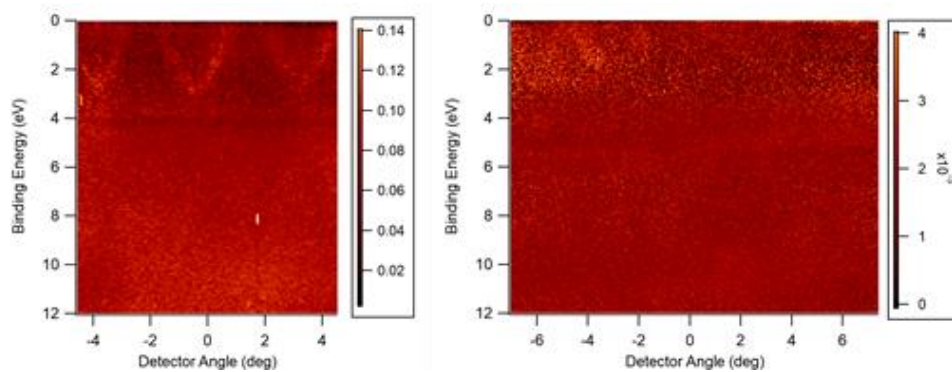


Figure SM-1: ARPES data, normalized by DOS and by XPD modulations: **a)** $h\nu = 2830$ eV and $T \approx 90$ K; **b)** $h\nu = 5953.4$ eV and $T \approx 300$ K.

SM-2 Calculated relative angular shift of the band structure features with respect to the x-ray photoelectron diffraction (XPD)

A relative angular shift of the band structure features with respect to the x-ray photoelectron diffraction (XPD) pattern in the detector image occurs due to the fact that in the hard x-ray regime the dipole approximation is no longer valid, and the effects of the photon momentum $k_{h\nu}$ on the magnitude and direction of the final photoelectron momentum k_f must be considered. This angular deflection is expected to be observed in the position of all band structure features in the detector image.[ref 31] The calculations below are for $h\nu=3237.5$ eV and $E_{kin}=h\nu$, which is valid for valence band electrons close to the Fermi edge. The magnitude of the final valence-band photoelectron momentum can be computed via

$$|\vec{k}_f| = 0.512 * E_{kin}^{1/2} = 29.19 A^{-1} \quad (\text{SM-2a})$$

The magnitude of the photon momentum is given by

$$|\vec{k}_{hv}| = 0.0005107 * E_{hv} = 1.64 A^{-1} \quad (\text{SM-2b})$$

Since in our experimental geometry the direction of the photoelectron momentum is perpendicular to the direction of the photon momentum, the angular deflection due to the photon momentum vector can be computed using

$$\Delta = \tan^{-1}(1.642 / 29.19) = 3.219 \text{ deg} \quad (\text{SM-2c})$$

SM-3 Free Electron Final State calculations (FEFS)

The **Free Electron Final State** (FEFS) model [ref.76] maps the momentum vector of the photoelectron in vacuum \mathbf{k}_f to its initial momentum state in the crystal \mathbf{k}_i before the photoexcitation. This is based on two assumptions. First, the FEFS model assumes that the momentum components parallel to the sample surface are conserved throughout the entire photoemission process. Second, the momentum component perpendicular to the surface is determined using energy conservation and using the empirical inner potential V_0 within the crystal:

$$E_f(\mathbf{k}_f) = E_i(\mathbf{k}_i) + hv = \frac{\hbar^2 k_f^2}{2m_e} - V_0 + \phi_s = \frac{\hbar^2 \mathbf{K}^2}{2m_e} + \phi_s \quad (\text{SM-3a})$$

and

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{k}_{hv} + \mathbf{g}_{hkl} \quad (\text{SM-3b})$$

where $E_f(\mathbf{k}_f)$ is the final electronic kinetic energy, $E_i(\mathbf{k}_i)$ is the initial energy relative to the Fermi energy, hv is the photon energy, m_e is the electron mass, ϕ_s is the work function, \mathbf{k}_i is the initial-state wave vector within the reduced Brillouin zone (BZ), \mathbf{k}_f is the final-state wave vector inside the crystal, \mathbf{K} is the wave vector of the photo emitted electron in vacuum, \mathbf{k}_{hv} is the wave vector of the photon, and \mathbf{g}_{hkl} is the bulk reciprocal lattice vector.

Figure 6c) shows a comparison of the FEFS calculation to HARPES data, and even despite some smearing, one can clearly see a good agreement between the calculated ‘‘bulk’’ band structure and the experimental HARPES image.

A particular challenge in HARPES experiments compared to conventional low-energy ARPES is the extreme sensitivity to the sample alignment. Due to the extreme length of the photoelectron momentum vector \mathbf{k}_f at photon energies of several keV, even misalignments in the order of 0.1 degrees result in a sizable displacement within the reduced Brillouin zone

scheme. Even though the sample was carefully aligned, we had to vary the sample geometry that was used for our calculations, and we found the best agreement after tilting the sample by 0.5 degrees compared to the initially assumed sample geometry. [ref. 77]

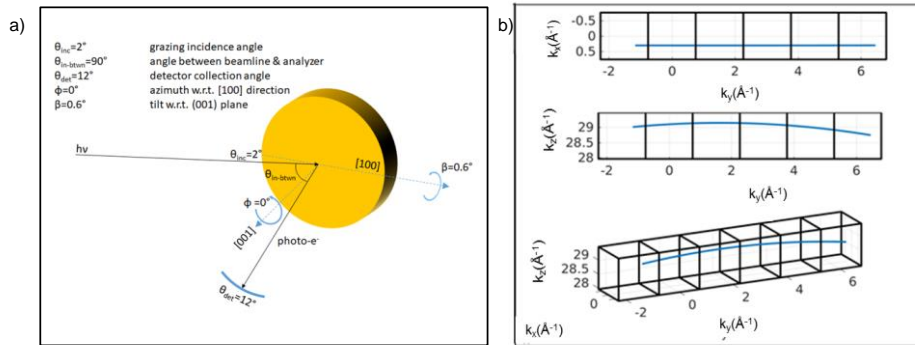
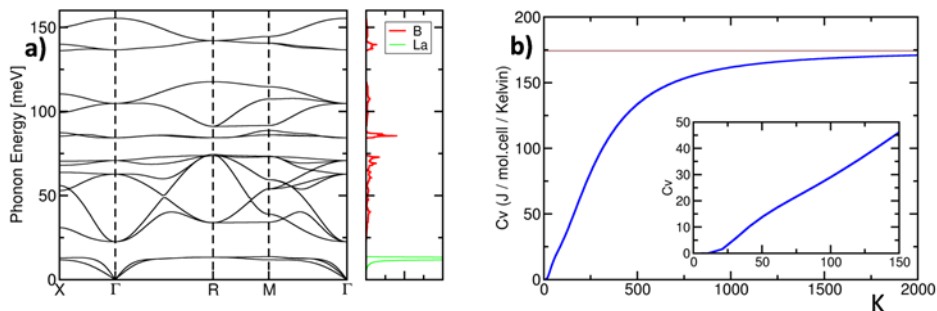


Figure SM-3: a) Geometry used in FEFS calculations; b) HARPES paths in k-space for the optimized experimental geometries determined from the FEFS calculations. The paths are shown in three different perspectives.

SM-4 Phonon band structure and specific heat of LaB₆



Figures: a) Phonon band structure of LaB₆ and b) Specific heat of LaB₆

Figure SM-4a) shows the phonon band structure of LaB₆, with element projected Density of States in side panel. Figure SM-4b) shows the specific heat of LaB₆ within the harmonic approximation and DFPT, as a function of temperature in Kelvin (K). Inset shows the small bump created by the Lanthanum manifold around 50 K. [ref 38,39,40,41,42,43,44,78]