Supporting Information for
Crystallization of heavy fermions via epitaxial strain in spinel LiV$_2$O$_4$
thin film.

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This PDF file includes:
- Supporting text
- Figures S1 to S5
Supporting Information Text

EELS data processing. The 3d states of V are probed via the V $L_{2,3}$ edges at 513 and 521 eV. A simple power law background subtraction was used and the multiple scattering was alleviated to minimize the effect of thickness for the $L_2/L_3$ ratio calculations as available in Digital Micrograph. No principal components analysis (PCA) or other noise-reducing data processing were employed. Due to the limited energy resolution (~0.7 eV) governed by the energy dispersion that we chose for a sufficiently high spectral signal-to-noise ratio, the delocalization of the inelastic electron scattering, as well as the experimental difficulty of calibrating the energy scales, we do not leverage the chemical shift but rather focus on the changes in the $L_2/L_3$ intensity ratio to determine the V valence. The V valence was determined by using the maximum intensities of the two peaks $I(L_2)/I(L_3)$ using the method of Ref. 1, since the continuum contribution cannot be removed due to the overlap with the O $K$ edge at ~532 eV.

For quantitative analysis, reference spectra for V$^{3+}$ and V$^{4+}$ from the literature (2) were used to confirm the expected V valence state of the LiV$_2$O$_4$ films, as shown in Fig. S4. The $L_2/L_3$ ratios are 0.83 and 1.02 for V$^{3+}$ and V$^{4+}$ spectra, respectively. We note that the potential intermixing of an inelastic EELS signal due to a delocalization effect could underestimate the valence states (3, 4).
Fig. S1. XRD characterization of a LiV$_2$O$_4$ thin film on STO using a Cu $K_\alpha$ source. (A) X-ray $\theta$-2$\theta$ scan of a LiV$_2$O$_4$ thin film on STO. The peak with the asterisk originates from the STO (002) reflection due to a minor Cu $K_\beta$ component. deg. and a.u. denote degree and arbitrary unit, respectively. (B) Rocking curve of the LiV$_2$O$_4$ (004) peak. The estimated full width at half maximum (FWHM) using a Pseudo-Voigt function is 0.728(1) deg. (C) X-ray reflectivity profile. From Kiessig oscillations, the film thickness is estimated to be 39.0(7) nm.
Fig. S2. XRD characterization of a LiV$_2$O$_4$ thin film on MgO using a Cu $K_α$ source. (A) X-ray $θ$-2$θ$ scan of a LiV$_2$O$_4$ thin film on MgO. The peaks with the asterisk originate from the MgO (002) and (004) reflections due to a minor Cu $K_α$ component. (B) Rocking curve of the LiV$_2$O$_4$ (004) peak. The estimated FWHM using a Pseudo-Voigt function is 0.0611(1) deg. (C) X-ray reflectivity profile. The film thickness is estimated to be 31.2(2) nm.
**Fig. S3.** Representative STEM-HAADF image of a LiV$_2$O$_4$ film on STO showing periodic misfit dislocations at the interface, which are indicated by the yellow arrows.
**Fig. S4.** Comparison of V valence states between the LiV$_2$O$_4$ film on STO and the reference spectra for V$^{3+}$ and V$^{4+}$. Vanadium $L_{2,3}$ spectrum for the LiV$_2$O$_4$ film on STO is averaged over all the spatially resolved data in Fig. 3B (blue). Two reference $L_{2,3}$ spectra for V$^{3+}$ and V$^{4+}$ obtained from the literature on V$_2$O$_3$ and VO$_2$ (2) are shown for comparison (black). The averaged LVO/STO spectrum appears as a 1:1 superposition of the V$^{3+}$ and V$^{4+}$ spectra: the $L_2/L_3$ ratio is ~0.9, close to an average of 0.83 for V$^{3+}$ and 1.02 for V$^{4+}$. 
Fig. S5. Spatial variation of the V L$_{2,3}$ edges in the LiV$_2$O$_4$ thin film on MgO. (A) STEM-HAADF image of the LiV$_2$O$_4$ film on MgO. The white arrow indicates the line of scanning on which the EELS spectra in (D) were acquired. The vertical line indicates the averaging width while scanning. (B) Simultaneously recorded annular dark-field (ADF) intensity profile does not show any appreciable changes in the intensity, ensuring no electronic modification under the beam. (C) Evolution of background-subtracted EELS line-scan spectra along the direction of the white arrow are shown in a gray scale, which indicate the two peaks at 513 and 521 eV corresponding to the V L$_3$ and L$_2$ white-lines, respectively. (D) V L$_{2,3}$ spectra collected from positions 1-9 in (A). Each spectrum is normalized to the L$_3$ edge intensity maximum, and vertically offset for clarity.
SI References

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