

# Supplemental Material for Clarifying the apparent flattening of the graphene band near the van Hove singularity

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## COMPUTATIONAL DETAILS

Theoretical calculations were performed using the Vienna ab-initio simulation package (VASP)[1], using the generalized gradient approximation in the revised Perdew-Burke-Ernzerhof version (PBEsol)[2] for the exchange-correlation energy. We used projected augmented-wave (PAW) pseudopotentials[3] for all the atomic species involved, with an energy cutoff up to 400 eV. The surfaces were simulated within a supercell approach considering 11 Co layers along the [0001] direction and about 12 Å of vacuum (11 Co layers are sufficient to ensure convergence). Graphene was adsorbed on the topmost Co surface layer in the  $1 \times 1$  reconstruction with the top-fcc stacking. The ferromagnetic (FM) solution, for the Co atoms, were considered in the calculations. Integration over the Brillouin Zone (BZ) was performed using uniform Monkhorst and Pack grid[4] of  $12 \times 12 \times 1$  for sampling BZ using a Gaussian smearing with  $\sigma = 0.05$  eV. Structural optimization was allowed for all the atoms except for the 6 Co layers further away from graphene (bulk-like) which are fixed to their experimental Co bulk positions (lattice parameter 2.507 Å).

## GRAPHENE GROWTH AND LI INTERCALATION PROCESS

The LEED pattern of the as grown Gr/Co/W(110) sample is reported in Fig. S1. The hexagonal graphene spots are exactly matching the cobalt ones, demonstrating an epitaxial match between the two surfaces.

In Fig. S2, we report the band dispersion along the  $\Gamma$  direction and the Fermi surfaces for the as grown Gr/Co sample, the sample after Li deposition at room temperature, and after annealing at 650 K. The graphene is strongly interacting with the cobalt substrate, and its band structure is barely recognizable in the as grown sample, see Fig. S2(a, e). In the data at 40 eV Fig. S2(b, f) it is possible to distinguish one branch of the well-known *mini-cone state* [5, 6]. Once intercalating and depositing Li on top, the graphene band structure is clearly recognisable, see Fig. S2(c, g). This is a clear indication for the formation of a Li layers in between graphene and Co substrate, since

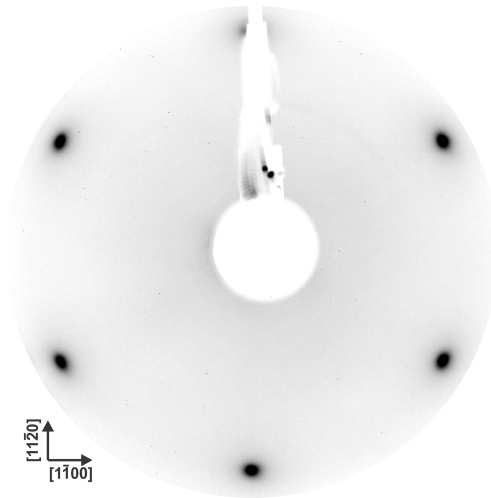


FIG. S1. LEED pattern of the Gr/Co(50 ML)/W(110) system acquired at  $E_k = 90$  eV, while keeping the sample at 80 K.

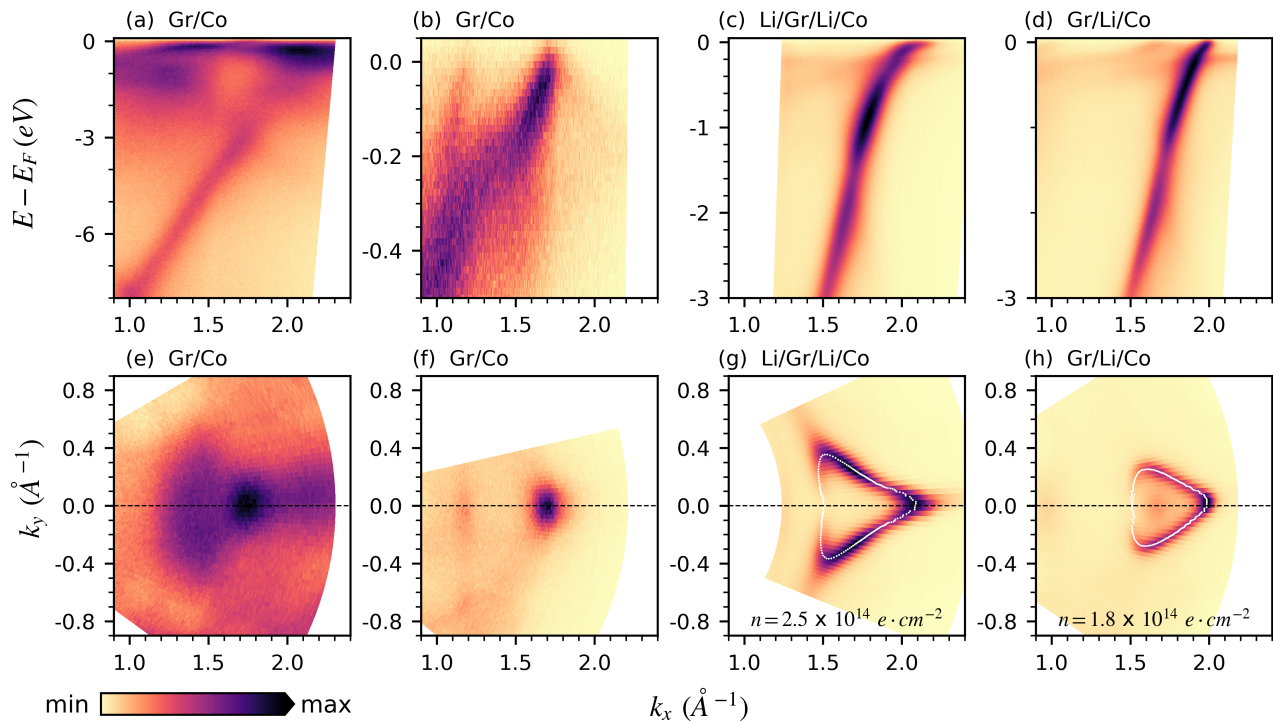


FIG. S2. Band dispersion along  $k_x$  direction [Fermi surface] for: the as growth Gr/Co using a photon energy of 70 eV (a) [(d)] and 40 eV (b) [(f)]; Li/Gr/Li/Co system as obtained after Li intercalation and on top deposition at 40 eV photon energy (c) [(g)]; Gr/Li/Co system as obtained after annealing at 650 K (d) [(h)]. The ARPES measurements were acquired at the VUV beamline, using p-polarization, while keeping the sample at 20 K. Data reported using a linear color scale.

only an intercalated Li layer can induce the graphene substrate detachment. After annealing at 650 K, S2(d, f), the system still shows a detached graphene layer, but with a reduced doping level of about  $1.8 \times 10^{14} e/cm^2$  rather than  $2.5 \times 10^{14} e/cm^2$ . In addition, we also noticed the reappearance of the *mini-cone states*, as probably due to the in-homogeneity of the probed region with a mixture of detached/non-detached graphene patches [7]. The doping level reduction after annealing, and also the higher doping level achievable with the further Li deposition keeping the sample at 80 K (as reported in the data of Fig. 2 and 3 of the main text), are a clear indication of the formation of an additional Li layer, which cannot be located anywhere else rather than on top of graphene.

It is important to note that the system reported in Fig. S2(c, g) was the one employed for the analysis of the electron-phonon kink in the main text. The spectrum was acquired at the VUV beamline, while keeping the sample at 20 K. As indicated from the Fermi surface analysis, there is a slightly lower level of electron doping as compared to the other data reported in the Fig. 2 and 3 of the main text ( $2.5 \times 10^{14} e/cm^2$  rather than  $3.6 \times 10^{14} e/cm^2$ ).

In Fig. S3, we report the atomic model and the corresponding calculated band structure of the Gr/Li/Co system, *i.e.* the system without the Li layer on top. The overall band structure is equivalent to the one with the additional Li layer on top apart from a reduced overall doping of the graphene layer.

### DOPING SATURATION LEVEL

The alkaline intercalation was followed by additional Li deposition for reaching the highest doping level. After this point, no additional electrons can be transferred to the graphene layer, and the deposited Li in excess gave only the detrimental effect of reducing the detectable signal from the carbon layer. In Fig. S4 we report the same data as in Fig. 2 of the main text, compared with the one after adding half more lithium than what was already present. The two systems MDC analyses are an excellent overlap, indicating that the saturation point is reached.

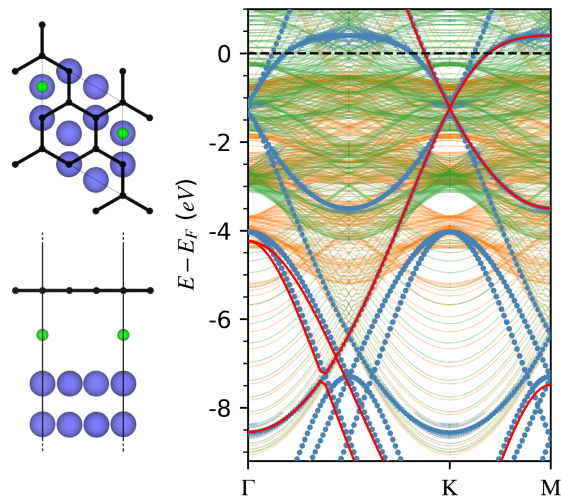


FIG. S3. On the left, atomic model of Li (green) intercalated graphene (black) supported by the Co substrate (blue). On the right, the spin-up (green) and spin-down (orange) electronic band structure for the overall system. Blue dots represents the carbon  $p_z$ -orbital weight for the states. Red line is the electronic band structure for an isolated graphene layer.

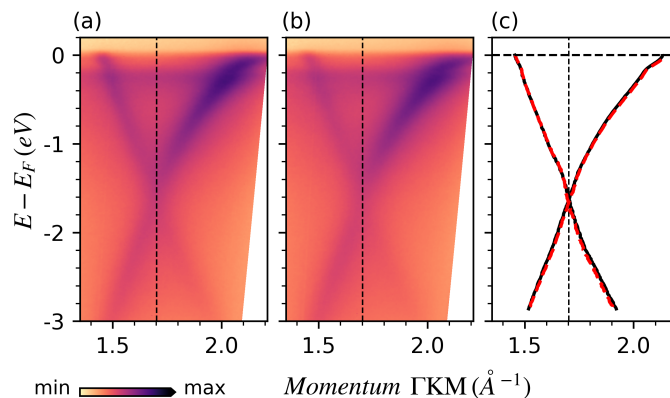


FIG. S4. Graphene Dirac cone dispersion along  $\Gamma$ KM direction of the Li/Gr/Li/Co system. Linear combination of the s- and p-polarization ARPES signals in the proximity of the Dirac point before (a) and after (b) additional half more Li than what already present (15 min deposition in (a) *vs.* 22 min deposition in (b)). Data reported using a square root color scale. (c) Extracted band dispersion from MDC analysis of the data in (a) and (b), reported as black lines and red dashed lines, respectively.

### POSSIBLE PRESENCE OF A POLARON BAND

In Fig. S5, we report the comparison between the ARPES signals from the clean cobalt substrate (50 ML Co on top of W(110)) before graphene growth, and the final system with graphene and lithium. The arrows point to the cobalt bands around -0.2 eV binding energy region. As mentioned in the main text, we are not able to distinguish the possible presence of a polaron band [8–10] due to the presence of such strong Co  $3d$  bands.

### ISO-ENERGY MAPS AROUND THE DIRAC POINT

In Fig. S6, we report different iso-energy maps for the data measured at BaDElPh with the relative iso-energy contours of the stretched PBEsol-DFT calculations. The theoretical agreement is excellent in each iso-energy map.

In Fig. S7, we report an analysis for the iso-energy map at -3.7 eV analogue to what proposed in Fig. 3 of the main text for the FS (iso-energy map at 0 eV). This particular map can be considered as the FS counterpart below the Dirac point. Because of the binding energy proximity with the  $\pi$ -band flattening at the M point, a similar signal from

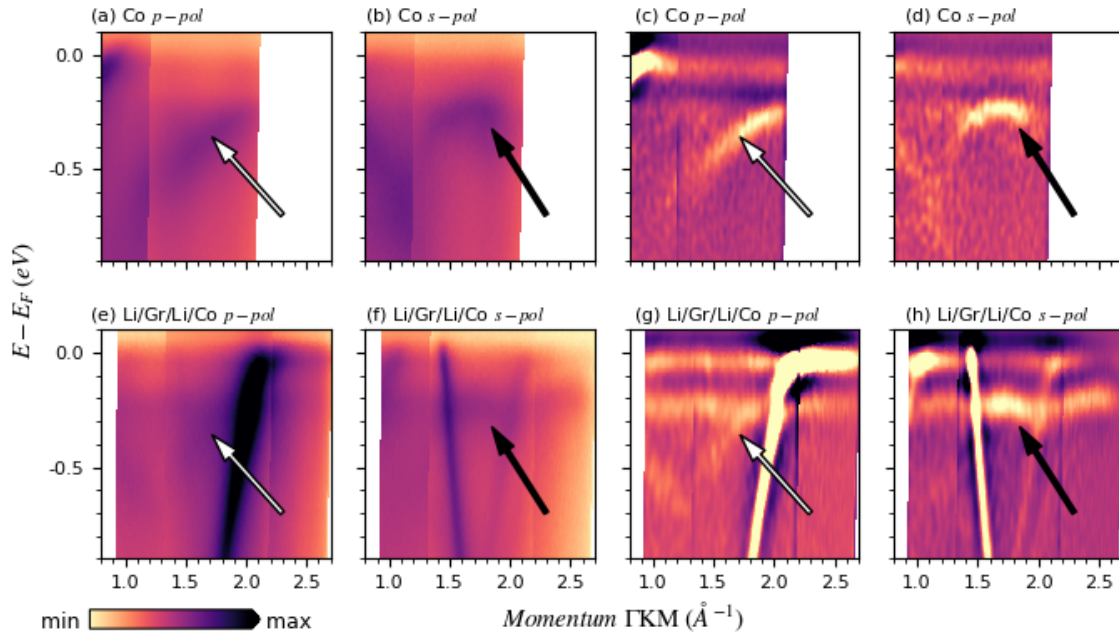


FIG. S5. (a),(b) Momentum maps, acquired with a photon energy of 33 eV and vertical and linear polarization respectively, along  $\Gamma K$  direction of the first BZ, of the 50 ML Co film deposited on W(110). (c),(d) Laplacian filtered maps of the ones in (a),(b). (e),(f) Momentum maps, acquired with a photon energy of 33 eV and vertical and linear polarization respectively, along  $\Gamma K$  direction of the first BZ, of the Li/Gr/Li/Co system. (g),(h) Laplacian filtered maps of the ones in (e),(f). The arrows indicate the Co 3d bands. A square root (linear) color scale used for reporting the data in (a), (b), (e) and (f) [(c), (d), (g) and (h)].

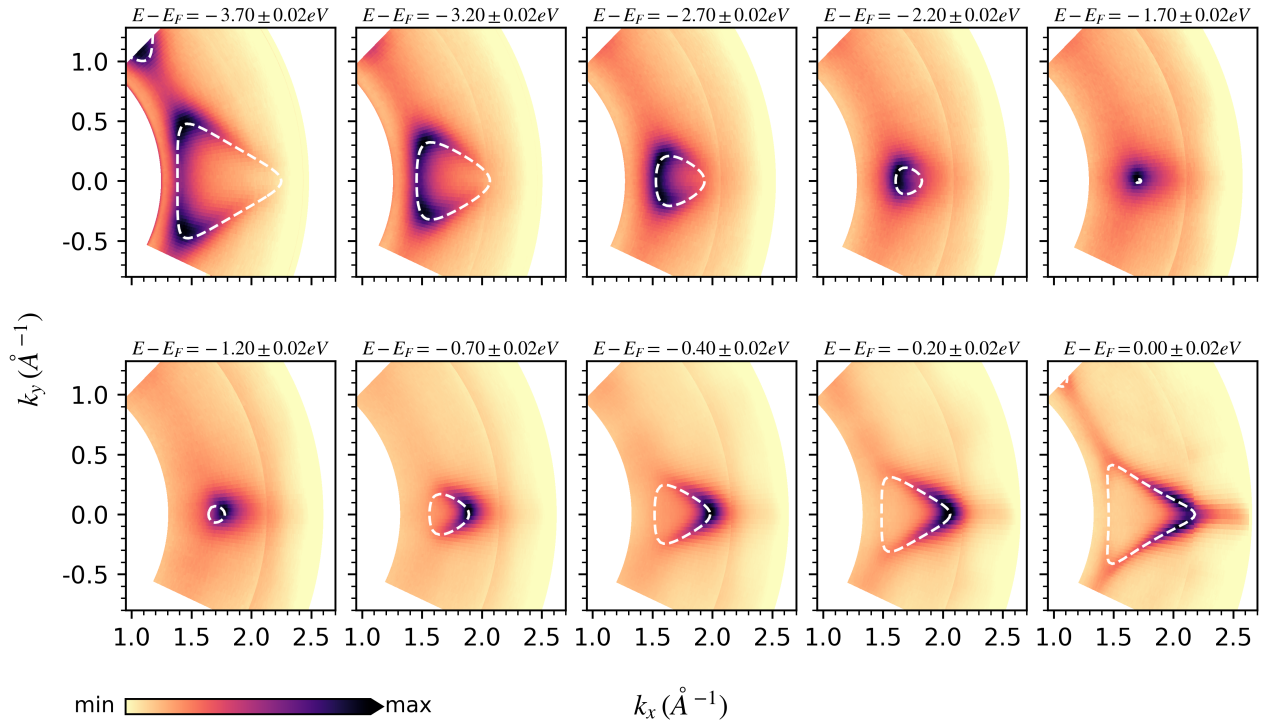


FIG. S6. Iso-energy maps of the Li/Gr/Li/Co system (from -3.7 to 0 eV) with the stretched (by 1.08 factor) PBE-sol DFT calculations (white dashed lines). Data reported using a linear color scale.

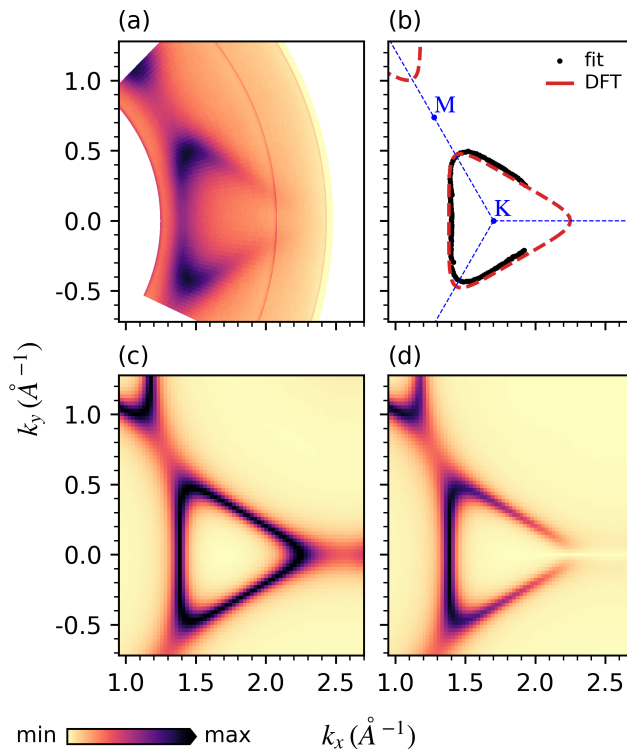


FIG. S7. Iso-energy map at -3.7 eV of the Li/Gr/Li/Co system. (a), ARPES spectra using p-polarization. (b), extracted band dispersion from MDC analysis (black dots) is reported with the stretched (by 1.08 factor) PBE-sol DFT calculations (red curve). Simulated spectral function, derived from the stretched DFT theoretical dispersion in (b), without (c) and with (d) the light polarization selection rules. Data reported using a linear color scale.

the spectral function “tail” is recognizable in the experimental data and well reproduced in the simulated spectra.

### WEIGHTED SIMULATED SIGNAL

The light polarization selection rules are reproduced in the simulated spectra by projecting all the calculated eigenfunction on two (incomplete) basis sets which are symmetric ( $\phi^+$ ) or antisymmetric ( $\phi^-$ ) with respect the mirror plane between the two carbon atoms of the graphene unit cell. These two sets are composed by only one function each, corresponding to the linear combination of the two  $p_z$  atomic orbitals belonging to the two different C sites in their local coordinate frame:

$$\begin{aligned} |\phi^+\rangle &= e^{ikR_1} |p_z^{C1}\rangle + e^{ikR_2} |p_z^{C2}\rangle, \\ |\phi^-\rangle &= e^{ikR_1} |p_z^{C1}\rangle - e^{ikR_2} |p_z^{C2}\rangle. \end{aligned} \quad (\text{S1})$$

The simulated intensity signal is then constructed from the contribution of each eigenstate  $\epsilon_{n,k}$  of the eigenfunction  $\psi_{n,k}$  weighted by the modulus square its projection on one of the two basis sets (depending on the light polarization), as:

$$W_{n,k}^\pm = |\langle \phi^\pm | \psi_{n,k} \rangle|^2. \quad (\text{S2})$$

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