I. DETAILS OF THE AB-INITIO CALCULATION

For the relaxation of crystal structures we used $6 \times 6 \times 6$ k-point grids within the GPAW code. The structure optimization process was controlled by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm implemented in the Python atomic simulation environment (ASE)\(^1\). We checked the remaining forces in the full potential local orbital code FPLO with a $12 \times 12 \times 12$ k-point mesh and found the atomic positions to be sufficiently converged. All further calculations using FPLO were carried out on $12 \times 12 \times 12$ k-point meshes.

We investigated the doping dependence of the electronic structure by means of the virtual crystal approximation (VCA). The VCA can be used to interpolate continuously between the properties of an atom with nuclear charge $Z$ and its neighbors in the periodic table of elements with nuclear charges $Z - 1$ or $Z + 1$. In the study presented here, we fractionally replaced nitrogen ($Z = 7$) by carbon ($Z = 6$). Because of the different valence of nitrogen and carbon this procedure interpolates between charge neutral ammonia (NH\(_3\)) and a methyl radical (CH\(_3\))\(^-\). As ammonia (NH\(_3\)) and methane (CH\(_4\)) are structurally similar, VCA should provide a sufficient description of the spacer layer.

II. DETAILS OF THE MODEL CONSTRUCTION

We obtained the low energy Hamiltonian for each doping level from ab-initio calculations and subsequent Wannier downfolding using the FPLO Wannier module. We keep all Fe $3d$ and Se $4p$ states in our models. For the 8 Fe supercell this process yields a 64 band tight binding model, which we then treat with the unfolding methods described in the main text. The energy window we used for the fit spans approximately from $-6$ eV to $+2$ eV.

In FPLO a direct unfolding of the DFT band weights is implemented\(^2\). We used it to check agreement between unfolded DFT band structure and unfolded model band structure in the 2 Fe picture to exclude uncertainties from the Wannierization procedure. The only case where we found small quantitative deviations close to the Fermi level is the Li\(_{0.5}(\text{NH}_2\text{H}_3)\text{Fe}_2\text{Se}_2\) compound, where a nitrogen band at $-1.5$ eV prevents a perfect fit using Fe $3d$ and Se $4p$ states only.

III. DETAILS OF THE SUSCEPTIBILITY AND PAIRING CALCULATION

The static susceptibility is calculated on a $30 \times 30 \times 10$ k-point mesh at an inverse temperature of $\beta = 40$ eV$^{-1}$. To calculate the pairing interaction, the susceptibility is
needed at k-vectors that do in general not lie on a grid. Those susceptibility values are obtained using trilinear interpolation of the gridded data.

The gap equation is solved using \( \sim 1000 \) points on the three-dimensional Fermi surface. Consequently the solution of the gap equation is available only on those points scattered in three-dimensional space. In order to obtain a graphical representation of the gap function on two-dimensional cuts through the Brillouin zone, we used multiscale radial basis function interpolation as implemented in ALGLIB (http://www.alglib.net).

As shown in Fig. 1, the nearest neighbor hopping \( t_1 \) is affected much stronger by the electron doping than the next-nearest neighbor hopping \( t_2 \). This behavior has been explained in the literature by the cancellation of direct and indirect hopping paths via the chalcogen atoms\(^3\). Recently, similar arguments were used to explain the doping dependence of superconductivity in LaFeAsO\(_1-x\)H\(_x\) and related materials\(^4\). In the intercalates we investigated, we find rather small Fe 3d\(_{xy}\) hoppings because of the large Se height of 1.476 Å, which reduces indirect hoppings via the Se atoms.

The band structure effects of changing individual hopping parameters have been worked out in great detail in Ref. 5. In the materials investigated here, the change in \( t_1 \) serves to shift the hole bands down (Fig. 2), which gives rise to the increased density of states at the Fermi level.

**IV. ROLE OF KINETIC FRUSTRATION**

An alternative way of understanding the variation in pairing strength with electron doping is provided through the analysis of the tight binding parameters. As mentioned in the main text, we observe a steep decrease of the nearest neighbor hopping with electron doping. To allow easy interpretation of the hopping elements, we constructed 5 band Fe only models by downfolding also the Se 4p states. We used an energy window ranging from \(-3\) eV to \(+2\) eV.

In Fig. 3 we plot the orbital resolved density of states for the 8 band model at \( r = 0.25 \). The positive slope close to the Fermi level and the edge of the hole bands at +0.1 eV are clearly visible.

**V. DENSITY OF STATES**

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