Unified picture of the doping dependence of superconducting transition temperatures in alkali metal/ammonia intercalated FeSe

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In the recently synthesized Li$_x$(NH$_2$)$_y$(NH$_3$)$_z$Fe$_2$Se$_2$ family of iron chalcogenides a molecular spacer consisting of lithium ions, lithium amide and ammonia separates layers of FeSe. It has been shown that upon variation of the chemical composition of the spacer layer, superconducting transition temperatures can reach $T_c \sim 44$ K, but the relative importance of the layer separation and effective doping to the $T_c$ enhancement is currently unclear. Using state of the art band structure unfolding techniques, we construct eight-orbital models from ab-initio density functional theory calculations for these materials. Within an RPA spin-fluctuation approach, we show that the electron doping enhances the superconducting pairing, which is of $s_\pm$-symmetry and explain the experimentally observed limit to $T_c$ in the molecular spacer intercalated FeSe class of materials.

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After the discovery of iron based superconductors in 2008, transition temperatures were quickly improved to $\sim 56$ K by chemical substitution [1]. Recently, the possible discovery of superconductivity with $T_c = 65$ K [2] and even $T_c \sim 100$ K [3] in single-layer FeSe films grown by molecular beam epitaxy on SrTiO$_3$ showed that temperatures close to and above the boiling point of liquid nitrogen (77 K) might be achievable. These results have initiated an extensive debate regarding the origin of the high superconducting temperatures and the role played by electron doping via substrate, dimensionality and lattice strain.

While bulk FeSe has a $T_c$ of only 8-10 K, it has been known for some time that it can be substantially enhanced, to 40 K or higher by alkali intercalation [4]. Materials with a single alkali A = K, Cs, Rb between FeSe layers of nominal form A$_2$Fe$_2$-Se$_2$ have been intensively studied, and shown to display a wide variety of unusual behaviors relative to the Fe pnictide superconducting materials [5]. These include likely phase separation into an insulating phase with block antiferromagnetism and ordered Fe vacancies, and a superconducting phase that is strongly alkali deficient and whose Fermi surface as measured by ARPES apparently contains no holelike Fermi surface pockets, in contrast to Fe-pnictides. Since the popular spin fluctuation scenario for $s_\pm$ pairing relies on near nesting of hole and electron pockets, it has been speculated that a different mechanism for pairing might be present in these materials, and even within the spin fluctuation approach, different gap symmetries including d-wave pairing have been proposed [6, 9]. The gap symmetry and structure is still controversial, however [10, 11].

In addition to the unusual doping, speculation on the origin of the higher $T_c$ has centered on the intriguing possibility that enhancing the FeSe layer spacing improves the two-dimensionality of the band structure and hence Fermi surface nesting [12, 13]. In an effort to investigate this latter effect, organic molecular complexes including alkalis were recently intercalated between the FeSe layers [12–19], yielding transition temperatures up to 46 K. The most intensively studied materials incorporate molecules including ammonia, for example Li$_{0.56}$(NH$_2$)$_{0.53}$(NH$_3$)$_{1.19}$Fe$_2$Se$_2$ with $T_c = 39$ K [14] and Li$_{0.6}$(NH$_2$)$_{0.2}$(NH$_3$)$_{0.8}$Fe$_2$Se$_2$ with $T_c = 44$ K [15]. The crystal structure of a stoichiometric version of these materials is shown in Fig. 1. Recently, Noji et al. [12] correlated data on a wide variety of FeSe intercalates and noted a strong correlation of $T_c$ with interlayer spacing, corresponding to a nearly linear increase between 5 to 9 Å, followed by a rough independence of spacing with further increase between 9 to 12 Å.

In the present work we study the question of how exactly doping and interlayer distance influence $T_c$ in molecular intercalates of FeSe, whether these effects are separable, and what gives rise to the apparent upper limit for $T_c$ in this family of iron chalcogenides. Using a combination of first principles calculations of the electronic structure of several materials in this class, together with model calculations of spin fluctuation pairing based on these band structures, we argue that strength and wavevector of spin-fluctuations in lithium/ammonia intercalated FeSe can be controlled by tuning the Li$^+$:NH$_2^-$ ratio in the spacer layer. We show that the evolution of $\bar{T}_c$ with electron doping can be understood from the shape of the density of states close to the Fermi level. As long as hole pockets are present, we find that the superconducting pairing is of $s_\pm$ character and identify a subleading $d_{x^2-y^2}$ instability. We believe that our interpretation is valid in a broad class of related materials.

We performed density functional theory calculations for Li$_{0.5}$(NH$_2$)$_{0.75}$(NH$_3$)$_{1.19}$Fe$_2$Se$_2$ at various ratios of NH$_2$ to NH$_3$ content, starting from the experimentally determined structures Li$_{0.56}$(NH$_2$)$_{0.53}$(NH$_3$)$_{1.19}$ and...
Li$_{0.6}$(NH$_2$)$_{0.2}$(NH$_3$)$_{0.8}$ [14], which include fractionally occupied atomic sites for lithium, hydrogen and nitrogen. In order to accommodate the experimental stoichiometry we construct a $2 \times 1 \times 1$ (4 Fe) supercell for the former, and a $2 \times 2 \times 1$ (8 Fe) supercell for the latter compound. We replace all fractionally occupied nitrogen positions by fully occupied positions. As hydrogen positions are not known precisely from experiment, we arrange the hydrogen atoms so that we obtain NH$_3$ groups with angles of about 108° as encountered in ammonia and further relax these positions within the local density approximation (LDA) [20] with the projector augmented wave (PAW) basis [22] as implemented in GPAW [23] until forces are below 2 meV/Å. In the $2 \times 1 \times 1$ supercell we place the lithium atom in one half of the unit cell and leave the lithium position in the other half unoccupied. In the $2 \times 2 \times 1$ supercell we arrange the lithium atoms in a chequerboard pattern of occupied and vacant sites (Fig. 1).

Initially, we only consider charge neutral NH$_3$ ammonia groups in the spacer and no NH$_2^-$ . In this way, we obtain idealized structures with formula units Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ and Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ where chalco-gen height and unit cell parameters are chosen as in the experimental structures [14, 15]. Both structures belong to the space group P1 because of NH$_3$ situated in the spacer layer. Note that by setting up both structures with neutral NH$_3$, we are able to disentangle possible effects of the structural differences from the effect of doping through the composition of the spacer layer.

The experimentally available samples [14, 15] contain both NH$_3$ and NH$_2^-$ . The radical NH$_2^-$ neutralizes the charge donated to the FeSe layer by Li$^+$ and reduces the doping level. In order to capture this compensation of charge in our simulations, we use the virtual crystal approximation (VCA) [24] starting from supercells Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ and Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$, which correspond to the maximally electron doped compounds. The use of VCA has the advantage that doping is treated in a continuous and rather isotropic, but not rigid band fashion. We checked these calculations by removing hydrogen atoms explicitly instead of doing VCA and found the differences to be negligible.

The analysis of the band structure of these supercells is done within an all electron full potential local orbital (FPLO) [25] basis and we use LDA as exchange-correlation functional [20]. We then use projective Wannier functions as implemented in FPLO [25] to downfold the band structure. In our tight binding models, we keep the Fe 3d and Se 4p states. In order to obtain band structure and Fermi surface of the supercells in the conventional two iron unit cell, we use our recently developed technique [26] to translationally unfold the 32 and 64 band supercell models to a 16 band model of the 2 Fe equivalent Brillouin zone. For calculations of susceptibility and superconducting pairing, we use subsequent glide reflection unfolding [26] of the bands to obtain the 8 band model of the 1 Fe equivalent Brillouin zone.

First we investigated the properties of the maximally electron doped compounds in our study, Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ (ammonia poor) and Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ (ammonia rich). Both feature at the Fermi level (not shown) two large electron pockets in the corners of the 2 Fe Brillouin zone and two small hole pockets around $\Gamma$. This confirms that the lithium atoms donate electrons to the FeSe layer. Both systems have the same electron doping but different interlayer spacing. This is observed in the $k_z$-dispersion of the Fermi surface, where the smaller interlayer distance of the ammonia poor compound leads to a slightly increased corrugation of the cylinders.

In the experimentally realized compounds Li$_{0.56}$(NH$_2$)$_{0.53}$(NH$_3$)$_{1.19}$ and Li$_{0.6}$(NH$_2$)$_{0.2}$(NH$_3$)$_{0.8}$ the spacer layer nominally donates a charge of 0.015 and 0.2 electrons per iron atom respectively. These
doping levels are lower than in our model materials Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ and Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$. To investigate the doping dependence of the electronic structure at a given interlayer spacing, we consider Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ and hole dope it by means of the virtual crystal approximation as explained above. To simplify the notation, we label compounds from now on by their full chemical formula, but by an index \( r = \{0.0, \ldots , 0.25\} \), which refers to the chemical formula Li$_{0.5}$(NH$_3$)$_{0.5-2r}$(NH$_2$)$_{0.5+2r}$Fe$_2$Se$_2$. \( r = 0.25 \) refers to the compound Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ with maximal electron doping, where lithium nominally transfers a quarter of an electron to each iron atom. Increasing the NH$_3^-$ content immediately brings up a third hole pocket to the Fermi level, which is three-dimensional at intermediate doping and becomes two-dimensional once the charge introduced by lithium is fully compensated by NH$_3^-$ groups. \( r = 0 \) denotes the compound where the charge introduced by lithium is nominally compensated by NH$_3^-$ and no electrons are donated to the FeSe layer. The Fermi surfaces of the end members (\( r = 0.0 \) and \( r = 0.25 \)) are shown in Fig. 2. The band structure on high-symmetry paths is included in the Supplemental Material 23.

Upon further analysis of the tight-binding parameters we find that the hole pockets do not only shrink because the electron doping raises the Fermi level, but also because the nearest neighbor hopping in the Fe 3d$_{xy}$ orbital decreases steeply as a function of electron doping. This near cancellation of direct and indirect hopping paths has been discussed in the literature for other iron based superconductors 27/29. In the materials investigated here, we find that the degree of localization in the Fe 3d$_{xy}$ orbital can be tuned with relatively low electron doping. Further information are given in the Supplemental Material 23.

Next, we investigate the doping dependence of spin fluctuations. The non-interacting static susceptibility on the high-symmetry path calculated in the 1-Fe Brillouin zone for \( r = 0.0 \) and \( r = 0.25 \) is shown in Fig. 3. The susceptibility \( \chi_{\nu \pi}^{ll} \) is a four-tensor in orbital indices. The observable static susceptibility is defined as the sum over all components \( \chi_{\nu \pi}^{ll} \). In the undoped compound (\( r = 0.0 \)) the structure of the static susceptibility resembles strongly what is found for materials like LaFeAsO or BaFe$_2$As$_2$. The electron doping notably shifts the maximum from \( X = (\pi, 0) \) towards \( M = (\pi, \pi) \) and the former valley at \( M \) transforms into a peak. The absence of a (\( \pi, 0 \)) peak in electron doped compounds suggests why no orthorhombic phase or stripe-like magnetism have been found in FeSe intercalates so far 23.

The shifts of the dominant vectors of spin fluctuations can be understood from nesting properties and orbital character on the Fermi surface in the 1-Fe Brillouin zone. The undoped compound (\( r = 0.0 \)) is dominated by (\( \pi, 0 \)) nesting of electron and hole pockets, whereas the electron doped compound (\( r = 0.25 \)) (see Fig. 4) features scattering between electron and hole pockets with altered wave vector competing with scattering between electron pockets. The dominant contributions to the static susceptibility originate from the d$_{xy}$ and d$_{xz/yz}$ orbitals.

To explore how the superconducting state might depend on interlayer spacing and doping, we use the 3D version of random phase approximation (RPA) spin fluctuation theory 31 with Hamiltonian \( H = H_0 + H_{\text{int}} \). Here \( H_0 \) is the tight-binding Hamiltonian derived from the DFT calculations using the projective Wannier function formalism described above, and \( H_{\text{int}} \) is the Hubbard-Hund interaction, including the onsite intra (inter) orbital Coulomb interaction \( U \) (\( U' \)), the Hund’s rule coupling \( J \) and the pair hopping energy \( J' \). We keep the selenium states in the entire calculation, but consider interactions only between Fe 3d states. We assume orbitally rotation-invariant interactions parameters \( U = 1.35\text{ eV} \),...
that electron doping leads to an enhanced susceptibility of states near the Fermi level is positive (Fig. 6 (b)) so an increased density of states at the Fermi level. For tentative enhancement of $T_c$ and found that the FeSe layer is moderately electron doped. The electron doping moves the Fermi level further by intercalation of larger molecules. Summarizing, we investigated the $\text{FeSe}_2$ family of FeSe intercalates and superconducting pairing strength as the doping approaches the edge of the hole bands, which appears as a sharp drop of the $d_{xy}$ DOS [23]. The small initial decrease of the pairing eigenvalue at low electron doping (Fig. 6 (a)) is a consequence of the degraded nesting.

Alternatively, when we keep the electron doping levels fixed to the same value and analyze only the interlayer spacing effect (structures Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ with $c = 8.1$ Å and Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ with $c = 10.3$ Å), we find that the Fermi surface turns completely two-dimensional for a $c$-axis length between 8.1 Å and 10.3 Å, where $T_c$ saturates in experiment. Analyzing the susceptibility and superconducting pairing for both structures, we find no qualitative differences. Quantitatively, the perfectly two-dimensional Fermi surface of the ammonia rich compound leads to an increased susceptibility and larger pairing eigenvalue than in the ammonia poor compound. The increased pairing eigenvalue would correspond to an enhanced $T_c$.

Our calculations show that both increasing electron doping and lattice spacing contribute to enhancing $T_c$. However, experimentally it is found that the ammonia poor compound (larger electron doping) with smaller $c$-axis shows a higher $T_c$ (Li$_{0.6}$(NH$_2$)$_{0.2}$(NH$_3$)$_{1.8}$Fe$_2$Se$_2$, $T_c = 44$ K) than the ammonia rich compound (smaller electron doping) with larger $c$-axis (Li$_{0.56}$(NH$_2$)$_{0.53}$(NH$_3$)$_{1.19}$Fe$_2$Se$_2$, $T_c = 39$ K). Therefore, the variations in lattice parameters observed experimentally cannot be the source of the enhancement of $T_c$. Within our picture, this leaves only the electron doping level as the controlling parameter. Hence we conclude that $T_c$ is mainly controlled by the electron doping level when the Fermi surface is mostly two-dimensional. Therefore it is unlikely that $T_c$ can be enhanced further by intercalation of larger molecules.

Summarizing, we investigated the Li$_x$(NH$_2$)$_y$(NH$_3$)$_{2-x}$Fe$_2$Se$_2$ family of FeSe intercalates and found that the FeSe layer is moderately electron doped. The electron doping moves the Fermi level towards the edge of the hole-bands, which gives rise to increased superconducting transition temperatures due to an increase in the density of states at the Fermi level.

$U' = U/2$, $J = J' = U/4$. The effective interaction in the singlet pairing channel is then constructed via the multiorbital RPA procedure. Both the original Hamiltonian and effective interaction are discussed, e.g. in Ref. 32.

For all values of electron doping (structures $r = 0.0$ to $r = 0.25$) and interlayer spacing (structures Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$ and Li$_{0.5}$(NH$_3$)$_2$Fe$_2$Se$_2$) considered we find the leading instability to be of nodeless $s_\pm$ character, while subleading solutions are of nodal $s_\pm$ and $d_{x^2-y^2}$ type (see Fig. 5 for structure $r = 0.25$). These are the leading states expected in the case of a nearly 2D system with both hole and electron pockets. Repulsive electron-hole $d_{xz/yz}$ and $d_{xy}$ interactions favor nodeless $s_\pm$ pairing, while interelectron pocket interactions, orbital weight variations around the Fermi surface, and intraband Coulomb interactions are known to frustrate the $s_\pm$ interaction and drive nodal behavior and eventually $d$-wave interactions when hole pockets disappear [8] [33].

We observe that the source of the moderate quantitative enhancement of $T_c$ with electron doping lies in an increased density of states at the Fermi level. For both the $d_{xy}$ and the $d_{xz/yz}$ orbitals the slope of density of states near the Fermi level is positive (Fig. 5 (b)) so that electron doping leads to an enhanced susceptibility and superconducting pairing strength as the doping approaches the edge of the hole bands, which appears as a sharp drop of the $d_{xy}$ DOS [23]. The small initial decrease of the pairing eigenvalue at low electron doping (Fig. 6 (a)) is a consequence of the degraded nesting.

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Summarizing, we investigated the Li$_x$(NH$_2$)$_y$(NH$_3$)$_{2-x}$Fe$_2$Se$_2$ family of FeSe intercalates and found that the FeSe layer is moderately electron doped. The electron doping moves the Fermi level towards the edge of the hole-bands, which gives rise to increased superconducting transition temperatures due to an increase in the density of states at the Fermi level.
level. We also showed that recently achieved interlayer distances in FeSe intercalates already produce a two-dimensional Fermi surface, which is optimal for $T_c$. Further experimental work should therefore concentrate on the charge doping through the spacer layer.

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Unified picture of the doping dependence of superconducting transition temperatures in alkali metal/ammonia intercalated FeSe: Supplemental Information

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I. DETAILS OF THE AB-INITIO CALCULATION

For the relaxation of crystal structures we used 6×6×6 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 12×12×12 k-point mesh and found the atomic positions to be sufficiently converged. All further calculations using FPLO were carried out on 12×12×12 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 \textit{ab-initio} calculations and subsequent Wannier downfolding using the FPLO Wannier module. We keep all Fe 3\(d\) and Se 4\(p\) 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\(_{0.5}\)(NH\(_2\)\(_{2.5}\))Fe\(_2\)Se\(_2\) (\(r = 0\)) compound, where a nitrogen band at \(-1.5\) eV prevents a perfect fit using Fe 3\(d\) and Se 4\(p\) states only.

III. DETAILS OF THE SUSCEPTIBILITY AND PAIRING CALCULATION

The static susceptibility is calculated on a 30×30×10 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).

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.

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 effect has been explained in the literature by the cancellation of direct and indirect hopping paths via the chalcogen atoms [3]. Recently this effect was also used to explain the doping dependence of superconductivity in LaFeAsO$_{1-x}$F$_x$ and related materials [4]. In the intercalates we investigated, we find rather small Fe 3$d_{xy}$ 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.

V. DENSITY OF STATES

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.

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